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Interim Guidelines for the Disposal/Destruction of PCBs and PCB Items by Non-Thermal Methods

TRW, Inc.
Redondo Beach, CA

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INTERIM GUIDELINES FOR THE DISPOSAL/DESTRUCTION OF PCBs AND PCB ITEMS BY NON-THERMAL METHODS

by

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The report is an interim resource and guideline document to help EPA regional offices implement the polychlorinated biphenyl (PCB) regulations (40 CFR 761) for using non-thermal methods of destroying/disposing of PCBs. The report describes and evaluates various alternative chemical, physical, and biological PCB removal and/or destruction technologies, including: carbon adsorption; catalytic dehydrochlorination; chlorinolysis; sodium-based dechlorination; photolytic and microwave plasma destruction; catalyzed wet-air oxidation; and activated sludge, trickling filter, and other bacterial methods. The alternative technologies were evaluated using technical, regulatory, environmental impact, economic, and energy criteria. Because the technologies investigated are in various stages of development (only sodium-based dechlorination is available commercially), data deficiencies exist and good engineering judgment was used to supplement available quantitative information. Of the technologies evaluated, many show potential for >90% PCB destruction with minimum environmental impact and low-to-moderate economic cost. These technologies are: catalytic dehydrochlorination, sodium-based dechlorination, and photolytic and microwave plasma processes.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Dechlorination	Pollution Control	13B	07A
Chlorine Aromatic Compounds	Sodium	Stationary Sources		
	Photolysis	Polychlorinated Biphenyls (PCBs)	07C	07E
Biphenyl	Microwaves			20N
Waste Disposal	Plasmas	Non-thermal Destruction		20I
Catalysis	Adsorption		07D	14G
Dehydrohalogenation		Dehydrochlorination		

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ABSTRACT

This report is an interim resource and guideline document intended to aid U.S. Environmental Protection Agency regional offices in implementing the PCB Regulations (40 CFR 761) with regard to the use of non-thermal methods for the destruction/disposal of PCBs.

The interim report provides descriptions and evaluates various alternative chemical, physical, and biological PCB removal and/or destruction technologies, including carbon adsorption, catalytic dehydrochlorination, chlorinolysis, sodium based dechlorinations, photolytic and microwave plasma destructions, catalyzed wet-air oxidation, and activated sludge, trickling filter and special bacterial methods.

Alternative destruction/disposal technologies were evaluated using technical, regulatory, environmental impact, economic, and energy requirements criteria. Because the technologies investigated are at various stages of development (only the sodium based dechlorination processes are now commercially available) data deficiencies exist, and good engineering judgement was used to supplement available quantitative information.

Of the technologies evaluated, numerous show the potential for greater than 90% PCB destruction with minimum environmental impacts and low to moderate economic costs. These technologies are catalytic dehydrochlorination, sodium-based dechlorinations, microwave plasma, and photolytic processes.

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1. INTRODUCTION

1.1 BACKGROUND

Polychlorinated biphenyls (PCBs) are derivatives of the compound biphenyl in which from one to ten of the hydrogens have been replaced with chlorine atoms. Because they are chlorinated and aromatic, PCBs are characterized by exceptionally high chemical and thermal stability. They are of moderate to low volatility (decreases with increasing chlorine content), are relatively non-flammable, stable to oxidation at elevated temperatures, and have excellent electrical insulating characteristics. PCBs are insoluble in water, are soluble in most common organic solvents, and are relatively non-hygroscopic.

PCBs are not naturally occurring. They are synthesized, and PCBs synthesized for commercial use are mixtures of various isomers. Although most individual PCB isomers are solids at room temperature, the mixtures are liquid and vary in consistency from mobile oils, to viscous fluids, to sticky resins. There are 209 possible PCB isomers, ranging from three monochloro isomers to one decachloro isomer (Hutzinger, et al., 1974). The commercial mixtures are very complex. Sissons and Welti (1970) identified 69 isomers in Aroclor 1254, a commercial mixture produced by Monsanto. The complexity of these mixtures makes the tasks of sampling and analysis difficult.

Monsanto was the major U.S. manufacturer of PCBs (Fuller, et al., 1976), and their trade mark was Aroclor. Each Aroclor mixture is named with a four digit number in which the first two digits, 12, indicate biphenyl as the percent compound, and the last two digits give the approximate weight percent of chlorine in the mixture. In the example above, the digits "54" in Aroclor 1254 indicate approximate 54 weight percent chlorine. Trademarks of other manufacturers and/or processors (world wide) are: Chlorextol, Allis-Chalmers, USA; Clophen, Farben Fabriken Bayer, Germany; Dykanol, Federal Pacific Electric

Co., USA; Fenclor, Caffaro S.P.A., Italy; Inerteen, Westinghouse Electric Corp., USA; Kanechlor, Kanegafuchi Chemical Industry Co., Japan; Noflamol, Wagner Electric Co., USA; Phenoclor and Pyralene, Prodlec, France; Pyranol, General Electric Co., USA; Santotherm, Mitsubishi-Monsanto, Japan; and Therminol, Monsanto, USA.

1.2 THE PROBLEM

There are three aspects of the PCB problem: their persistence, ubiquitousness, and health effects. The excellent chemical and thermal stability characteristics of PCBs made them quite useful in numerous commercial applications, particularly dielectric fluids in capacitors and transformers, but also in heat transfer and hydraulic systems, pigments, plasticizers, carbonless copying paper, electromagnets, components of cutting oils, and other uses. Their wide use and a lack of recognition of their hazards have led to PCBs being ubiquitously distributed world-wide in all compartments of the environment (Fuller, et al., 1976). Highest concentrations are typically found in industrialized areas, but PCBs are found in air, water, soil, and marine samples in remote, unindustrialized areas. Experimental evidence summarized by Fuller, et al., (1976), indicates that atmospheric transport is the major means by which PCBs have been so widely dispersed.

The second aspect of the problem is the large amount of PCBs produced, disposed of, and still in service. Fuller, et al., (1976), estimated that over 400,000 metric tons (mt) were sold domestically in the U.S. during the period 1957-1974. Nisbet and Sarofim (1972) estimated that cumulative sales of PCBs in North America amounted to 450,000 mt from 1930 to 1970 and that an estimated 354,000 mt had been released to the environment. Thus, as of 1970, some 96,000 metric tons are estimated to have been in service. Estimated domestic sales from 1971 through 1974 were 60,000 mt (Fuller, et al., 1976). Assuming no loss of this latter production (note that in 1972 Monsanto restricted sales to long-lived capacitor and transformer uses), it is estimated that 156,000 (96,000 + 60,000) metric tons of PCBs may still be in service. The Electric Power Research Institute estimates that a minimum of 121,400 mt of PCBs in utility capacitors exists and will require disposal over the next 40 years (EPRI 1979a). EPA (1976) estimated that

60 percent of the total production of 568,000 mt or 341,000 metric tons are still in service.

As noted above, Nisbet and Sarofim (1972) estimated that from 1930 to 1970, an estimated 354,000 metric tons of PCBs were released to the environment, distributed as follows:

- Air - 27,000 metric tons
- Fresh and coastal waters - 54,000 metric tons
- Dumps and landfills - 270,000 metric tons

EPA (1976) estimated that, up to and including 1975, between 136,000 and 181,000 metric tons of PCBs had entered the environment. While the estimates above vary, there is no question that large amounts of PCBs have been both introduced into the environment and await disposal.

The third aspect of the problem is that they are known to cause a variety of adverse health effects in humans, animals, and other organisms. The toxicology literature on PCBs has been summarized by Fuller, et al., 1976; Kornreich, et al., 1976; and EPA 1979. PCBs are poorly metabolized and tend to accumulate in organisms, particularly in body fat and lipid-rich organs and tissues. PCBs bioaccumulate and biomagnify. PCBs appear to have caused malignant and benign tumors in rats and mice. There are limited human epidemiological data, but excess carcinogenic effects have been observed in several large groups of persons exposed to PCBs. Several studies in laboratory animals have shown that PCBs cause fetal resorption, birth defects, and high offspring mortality rates at levels of 1-5 mg/kg body weight. There is also evidence that PCBs produce immuno-suppressive effects in laboratory animals.

Adverse effects observed in laboratory animals also occur in wild animals. Effects noted in mink fed PCB-contaminated fish included reproductive failure, reduced weight gain, increased mortality, and enlargement of liver, kidneys, and heart. PCBs are extremely toxic to several species of aquatic invertebrates and fish. Aroclor 1254 is toxic to several shrimp species at levels of about 1 ppb. Increased mortality of sheepshead minnows was observed in water containing 0.16 ppb of Aroclor 1254. Concentrations of Aroclors 1242, 1016, and 1254 as low as 0.1 ppb have been demonstrated to depress photosynthetic activity in phytoplankton.

The realization of the widespread distribution of PCBs in the environment and growing knowledge of their hazards led Monsanto in 1972 voluntarily to restrict sales of PCBs to the manufacture of electrical transformers and capacitors. Monsanto ceased all production in 1977.

Growing evidence of the problem of PCB contamination and disposal led to the inclusion of Section 6(e) in the Toxic Substances Control Act (TSCA) of 1976. Section 6(e) would require the eventual elimination of the use of PCBs in the United States.

Section 6(e) of TSCA required EPA to regulate the marking and disposal of PCBs in use. It provided for a ban on the manufacture and use of PCBs in other than a totally enclosed manner by 1 January 1978, a complete ban on manufacture by 2 July 1979, and a complete ban on distribution in commerce and processing by 1 July 1979. The latter bans included activities conducted in a totally enclosed manner. EPA was, however, authorized to grant exceptions to the ban rules under certain conditions. Regulatory implementation of Section 6(e) is summarized in EPA, 1979.

On 31 May 1979, (44 FR 31514) EPA promulgated the final rule, Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions (PCB Regulations). The PCB Regulations: 1) prohibit all manufacturing of PCBs after 2 July 1979; 2) prohibit processing, distribution in commerce, and use of PCBs except in a totally enclosed manner after 1 July 1979; and 3) authorize certain exemptions. The PCB Regulations do not require removal of PCBs and PCB Items from service and disposal earlier than would normally be required. But, when PCBs and PCB Items are removed from service, disposal must be in acceptance with the PCB Regulations which apply to any substance, mixture, or item containing greater than 50 ppm PCBs.

The Electric Power Research Institute concludes that there will be a shortfall of utility waste PCB disposal capacity (landfill and incinerator) in most EPA regions after 1 January 1980. While utilities apparently have the majority of PCB production still in service, there are numerous other commercial and industrial sectors also having PCBs still in service. Thus, there is a disposal problem, and this resource document was prepared, in part, to help ameliorate this disposal problem by providing implementation guidance and enhancing the review, approval, and permitting of alternative disposal methods contemplated by the PCB Regulations.

1.3 PURPOSE OF REPORT

This report is a resource and interim guidelines document. It is intended to aid EPA Regional Offices in evaluating facilities for which owners/operators have applied for approval for disposal/destruction of PCBs by "other approved methods", i.e., methods other than those for which the PCB Regulations give technical guidelines. To achieve this purpose, this report provides guidance in:

- Interpreting those portions of the PCB Regulations providing for thermal destruction
- Interpreting those portions of the PCB Regulations providing for disposal by means other than thermal destruction
- Establishing criteria for evaluating alternate disposal technologies and for evaluating the consistency of alternative disposal operations with the PCB Regulations
- Facilitating coordinated and comprehensive Agency review of PCB disposal operations

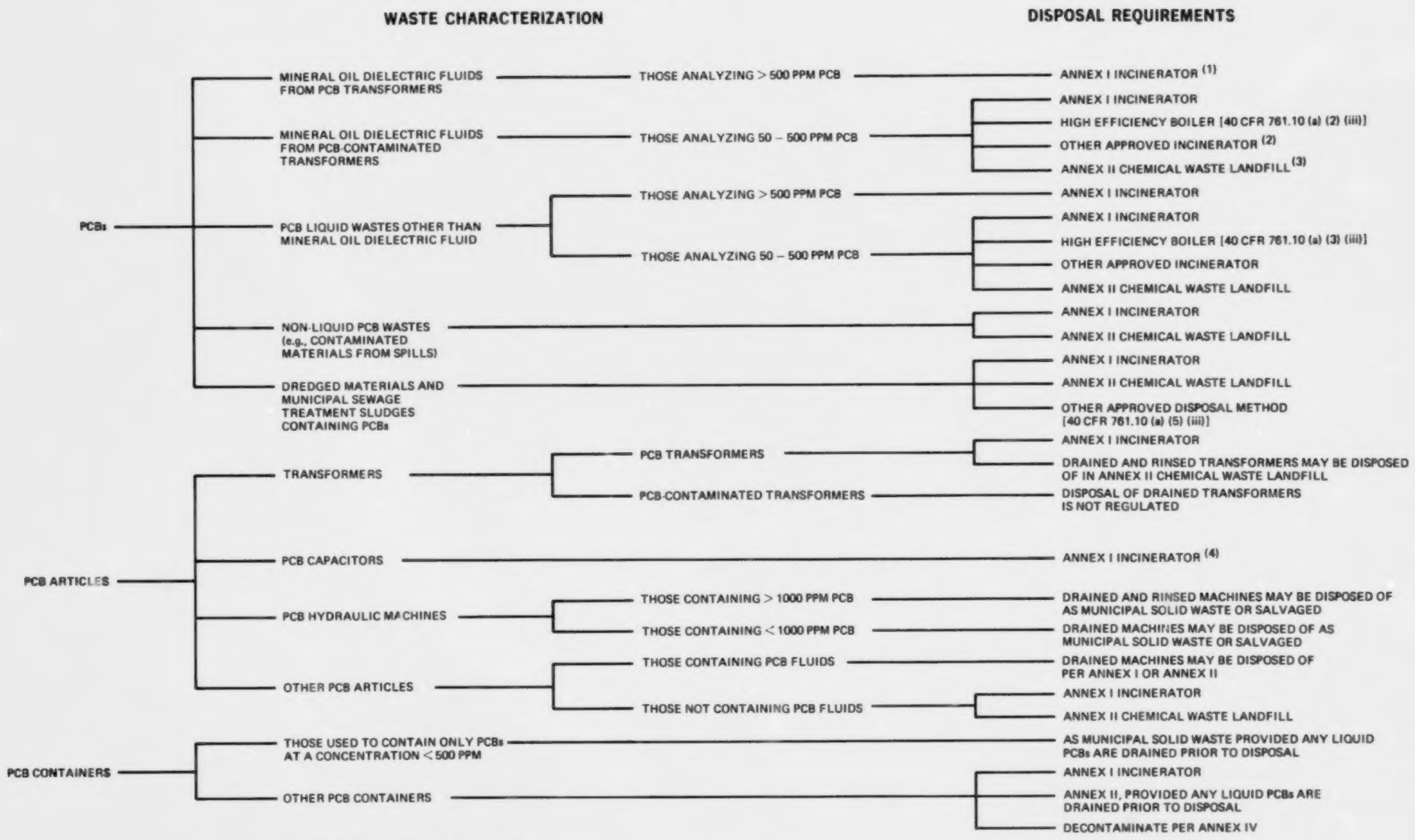
1.4 SCOPE OF REPORT

The PCB Regulations provide for disposal of PCB and PCB Items by:

- Incineration in Annex I incinerators (more specifically, in those incinerators meeting the requirements of Annex I)
- Incineration in high efficiency boilers
- Landfilling in Annex II chemical waste landfills

Figure 1 illustrates the allowable disposal methods. The PCB Regulations, Section 761.10(e), also provide for use of disposal/destruction technologies other than those listed above, provided certain requirements are met.

This interim guidelines document applies solely to disposal/destruction of PCBs by means other than Annex I incinerators or high efficiency boilers, Annex II chemical waste landfills, or as municipal solid waste.


WASTE CHARACTERIZATION
DISPOSAL REQUIREMENTS
PCBs
MINERAL OIL DIELECTRIC FLUIDS FROM PCB TRANSFORMERS
THOSE ANALYZING > 500 PPM PCB
ANNEX I INCINERATOR (1)
MINERAL OIL DIELECTRIC FLUIDS FROM PCB-CONTAMINATED TRANSFORMERS
THOSE ANALYZING 50 – 500 PPM PCB
ANNEX I INCINERATOR
HIGH EFFICIENCY BOILER [40 CFR 761.10 (a) (2) (iii)]
OTHER APPROVED INCINERATOR (2)
ANNEX II CHEMICAL WASTE LANDFILL (3)
PCB LIQUID WASTES OTHER THAN MINERAL OIL DIELECTRIC FLUID
THOSE ANALYZING > 500 PPM PCB
ANNEX I INCINERATOR
THOSE ANALYZING 50 – 500 PPM PCB
ANNEX I INCINERATOR
HIGH EFFICIENCY BOILER [40 CFR 761.10 (a) (3) (iii)]
OTHER APPROVED INCINERATOR
ANNEX II CHEMICAL WASTE LANDFILL
NON-LIQUID PCB WASTES (e.g., CONTAMINATED MATERIALS FROM SPILLS)
ANNEX I INCINERATOR
ANNEX II CHEMICAL WASTE LANDFILL
DREDGED MATERIALS AND MUNICIPAL SEWAGE TREATMENT SLUDGES CONTAINING PCBs
ANNEX I INCINERATOR
ANNEX II CHEMICAL WASTE LANDFILL
OTHER APPROVED DISPOSAL METHOD [40 CFR 761.10 (a) (5) (iii)]
PCB ARTICLES
TRANSFORMERS
PCB TRANSFORMERS
ANNEX I INCINERATOR
DRAINED AND RINSED TRANSFORMERS MAY BE DISPOSED OF IN ANNEX II CHEMICAL WASTE LANDFILL
PCB-CONTAMINATED TRANSFORMERS
DISPOSAL OF DRAINED TRANSFORMERS IS NOT REGULATED
PCB CAPACITORS
ANNEX I INCINERATOR (4)
PCB HYDRAULIC MACHINES
THOSE CONTAINING > 1000 PPM PCB
DRAINED AND RINSED MACHINES MAY BE DISPOSED OF AS MUNICIPAL SOLID WASTE OR SALVAGED
THOSE CONTAINING < 1000 PPM PCB
DRAINED MACHINES MAY BE DISPOSED OF AS MUNICIPAL SOLID WASTE OR SALVAGED
OTHER PCB ARTICLES
THOSE CONTAINING PCB FLUIDS
DRAINED MACHINES MAY BE DISPOSED OF PER ANNEX I OR ANNEX II
THOSE NOT CONTAINING PCB FLUIDS
ANNEX I INCINERATOR
ANNEX II CHEMICAL WASTE LANDFILL
PCB CONTAINERS
THOSE USED TO CONTAIN ONLY PCBs AT A CONCENTRATION < 500 PPM
AS MUNICIPAL SOLID WASTE PROVIDED ANY LIQUID PCBs ARE DRAINED PRIOR TO DISPOSAL
OTHER PCB CONTAINERS
ANNEX I INCINERATOR
ANNEX II, PROVIDED ANY LIQUID PCBs ARE DRAINED PRIOR TO DISPOSAL
DECONTAMINATE PER ANNEX IV

(1) ANNEX I INCINERATOR IS DEFINED AT 40 CFR 761.40.

(2) REQUIREMENTS FOR OTHER APPROVED INCINERATORS ARE DEFINED AT 40 CFR 761.10 (e).

(3) ANNEX II CHEMICAL WASTE LANDFILLS ARE DESCRIBED AT 40 CFR 176.41. ANNEX II DISPOSAL IS PERMITTED IF THE PCB WASTE ANALYZES LESS THAN 500 PPM PBC AND IS NOT IGNITABLE AS PER 40 CFR PART 761.41 (b) (8) (iii).

(4) DISPOSAL OF CONTAINERIZED CAPACITORS IN ANNEX II LANDFILLS IS PERMITTED UNTIL MARCH 1, 1981. THEREAFTER, ONLY ANNEX I INCINERATION IS PERMITTED.

Figure 1. Disposal requirements for PCBs and PCB Items.

Chapter 2 of this report develops criteria for evaluating alternative technologies. Chapter 3 describes alternative physiochemical and biological disposal technologies. Chapters 4 and 5 present, evaluations of alternative physicochemical and biological disposal methods, respectively. Chapter 6 presents a comparison of thermal and non-thermal means of disposal.

2. DEVELOPMENT OF EVALUATION CRITERIA

Chapter 2 will develop and describe criteria for evaluating non-thermal PCB disposal processes. The term "non-thermal" is used in the sense that it refers to disposal processes that do not rely on combustion to destroy PCBs. Guidelines for evaluating combustion processes, i.e., Annex I incinerators and high efficiency boilers, are described in Ackerman, et al., (1980).

The evaluation criteria are grouped into five general categories, each of which is described in subsequent sections. These categories are:

- Regulatory factors
- Technical factors
- Environmental factors
- Economic factors
- Energy factors

Each category must be considered in an overall evaluation although with cognizance that the regulatory factors category, especially regulatory requirements, is the most important one. Within a given category, individual evaluation criteria must be considered.

This chapter develops generic evaluation criteria, that is, criteria independent of specific non-thermal disposal practices. The purpose of this approach is to permit Regional Offices to make relative evaluations of various non-thermal disposal practices.

2.1 REGULATORY FACTORS

The siting and operation of a non-thermal PCB disposal facility must comply with applicable Federal, State, and local regulations. Table 1 is an overview of the most pertinent Federal statutes and regulations. Subsequent sections describe pertinent Federal regulations.

TABLE 1. FEDERAL LAWS/REGULATIONS PERTAINING TO PCBs

Federal Statute	Federal Regulation
Toxic Substances Control Act (TSCA)	EPA, 40 CFR 761, Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions
Clean Water Act (CWA)	EPA, 40 CFR 129, Toxic Pollutant Effluent Standards
Clean Water Act	EPA, 40 CFR 116, Designation of Hazardous Substances
Clear Air Act (CAA)	EPA, 40 CFR 51 & 52, Prevention of Significant Air Quality Deterioration
Resource Conservation & Recovery Act (RCRA)	EPA, 40 CFR 122-124 and 260-265, Hazardous Waste Guidelines and Regulations
Williams-Steiger Occupational Safety (OSHA) & Health Act	OSHA, 29 CFR 1910, OSHA Safety and Health Standards
Hazardous Materials Transportation Act (HMTA)	DOT, 49 CFR 171-177, Transportation of Hazardous Waste Materials
	EPA, Proposed Policy on Public Participation, 45 FR 28912

2.1.1 The PCB Regulations

Section 761.10 of the PCB Regulations specifies PCB disposal requirements. As shown in Figure 1, disposal of PCBs and PCB Items must be accomplished as follows:

- Mineral oil dielectric fluid from PCB-Contaminated Transformers containing 50 ppm or greater but less than 500 ppm PCBs, disposal through use of
    - Annex I incinerator
    - Annex II chemical waste landfill
    - High efficiency boiler
    - Other approved method
- Liquids other than mineral oil dielectric fluids containing 50 ppm or greater but less than 500 ppm PCBs, disposal through use of
    - Annex I incinerator
    - Annex II chemical waste landfill
    - High efficiency boiler
    - Other approved method
- Non-liquid PCBs in the form of contaminated soil, rags, or other debris, disposal through use of
    - Annex I incinerator
    - Annex II chemical waste landfill
    - Other approved method
- Dredged materials and municipal sewage treatment sludges that contain PCBs, disposal through use of
    - Annex I incinerator
    - Annex II chemical waste landfill
    - Other approved method

Section 761.10(e) provides for alternate disposal methods for PCBs or PCB Items that must be incinerated:

> Any person who is required to incinerate any PCBs and PCB Items under this subpart and who can demonstrate that an alternative method of destroying PCBs and PCB Items exists and that this alternative method can achieve a level of performance equivalent

> to Annex I incinerators or high efficiency boilers are provided in Sections 761.10(a)(2)(iv) and 761.10(a)(3)(iv) may submit a written request to the Regional Administrator for an exemption from the incineration requirements of Annex I. The applicant must show that his method of destroying PCBs will not present an unreasonable risk of injury to health or the environment. On the basis of such information and any available information, the Regional Administrator may, in his discretion, approve the use of the alternate if he finds that the alternate disposal method provides PCB destruction equivalent to disposal in an Annex I incinerator and will not present an unreasonable risk of injury to health or the environment. Any approval must be stated in writing and may contain such conditions and provisions as the Regional Administrator deems appropriate. The persons to whom such a waiver is issued must comply with all limitations contained in such determination.

Thus, the Regional Administrator must be able to evaluate whether the alternative system provides PCB destruction "equivalent" to Annex I incineration and whether the alternative will not present an unreasonable risk of injury to health or the environment before he issues an approval under this authority (761.10(e)). The key word in the regulation is "equivalent". The use of "equivalent" implies consideration of a variety of factors. The word "equal" is specifically not used in order to allow Regional Offices to use discretion in approving alternative methods.

The primary basis for evaluating an alternative method for PCB disposal is its performance relative to thermal methods. However, relative performance is not the only basis because Section 761.10(e) does not specify performance criteria. The Preamble to the PCB Regulations expresses EPA's expectation that Annex I incinerators will achieve destruction efficiencies of 99.9999 percent and high efficiency boilers would achieve destruction efficiencies of 99.9 percent or greater. These percentages provide general guidance as to expected destruction efficiencies. However, the use of flexible language in the rule rather than specific destruction efficiency values indicates that destruction efficiencies is not the only factor to be considered in determining equivalence.

The use of flexible language is based on several considerations relevant to evaluating alternative destruction/disposal methods:

- The PCB Regulations use the term "destruction efficiency as a measure of the difference between the amount of PCBs fed to a combustion system and the amount emitted to the air. This definition is relevant to the evaluation of boilers and incinerators but is irrelevant to the evaluation of a chemical process that has no air emissions.
- Sampling and analysis methods are subject to technical limitations that could cause an apparent failure to meet a specific "destruction efficiency" requirement.
- Treatment and control technologies for process effluent streams from potential disposal technologies are not equally well developed.

Sampling and analysis methodologies are both sciences and arts. They are sciences in that there is a body of validated methods for sampling and analysis of organic compounds, including PCBs. They are arts in that no one technique is optimum for sampling all streams or analyzing all samples. Thus, mandating a minimum acceptable destruction efficiency might: 1) give rise to situations where sampling and analysis techniques would be inadequate to demonstrate the required destruction efficiency, 2) cause delays and increased expense in modifying sampling and analysis methods for particular sites or samples, and 3) give rise to difficulties in comparing the effectiveness of different incinerators when different sampling and analysis methods were used.

The most difficult process stream to control is the stack gas because it is the most voluminous of the three generic streams and because none of the standard pollution control devices are effective in controlling organic vapor emissions. The PCB Regulations set a limit on maximum PCB emissions to the air from the stack gas (1 mg PCBs per kg of PCBs fed) while burning non-liquid PCBs (761.40(b)(1)). No limit was set for stack gas emissions during incineration of liquid PCBs. However, non-liquid PCBs are typically more difficult to incinerate than liquid PCBs, so that there is a higher probability of greater stack gas emissions of PCBs during incineration of non-liquid PCBs. Thus, an Annex I incinerator that can achieve stack gas emissions of PCBs of less than 1 mg per kg fed while burning non-liquid PCBs has a high probability of producing considerably lower PCB emissions while burning liquid PCBs.

The scrubber effluent is easier to control than the stack gas because it is less voluminous, it is a liquid rather than a gas, and because there are treatment methods effective at removing organic compounds. Further, because the scrubber is downstream of the combustion chamber(s), the scrubber solution comes into contact with only trace or undetectable levels of unburned PCBs. An explicit limit on the PCB content of the scrubber effluent is not given in the PCB Regulations. However, it is required (761.40(a)(9)) that the scrubber effluent be monitored and that it comply with applicable effluent or pretreatment standards (National Pollutant Discharge Elimination System permits) and any other state and Federal laws and regulations. Thus, other regulatory schemes set limits on PCB emissions in liquid process streams to the environment from Annex I incinerators.

If present,the solid residue effluent stream from an incinerator is the easiest to control because it is solid and the least voluminous. Therefore, no explicit limits on the PCB content of the solid residue streams is given, and there is no reference to any applicable regulatory criteria. However, it is a reasonable inference that the PCB Regulations govern disposal of this type of stream. Thus, if the solid residue stream contains less than 50 ppm PCBs, its disposal is not governed by the PCB Regulations. Conversely, if the solid residue stream contains 50 ppm or greater PCBs, its disposal is governed by the PCB Regulations: that is, disposal in an Annex I incinerator, Annex II chemical waste landfill, or other approved method.

A summary of the performance requirements for an Annex I incinerator (Section 761.40) follows:

- Gaseous effluent stream - 1 mg PCBs out per kg PCBs fed for non-liquid PCBs or 99.9999 percent gas phase destruction efficiency. A gas phase destruction efficiency requirement of 99.9999 percent while burning liquid PCBs is implied.
- Liquid effluent stream - As stated earlier, no explicit emission levels are given, but emissions of treated scrubber effluent from the site must conform to other Federal/State regulations, chiefly National Pollution Discharge Elimination System (NPDES) permits. Several relevant criteria are:
    - Protection of freshwater aquatic life: 1.5 ng/l (ng = 10^{-9}g) as a 24-hour average and a not to exceed value of 6.2 μg/l (μg=10^{-6}g) (EPA, 1978)

  - Protection of marine aquatic life: 24 ng/l as a 24-hour average and a not to exceed value of 0.2 μg/l (EPA, 1978)
  - Criteria for PCBs in navigable waters: 1 μg/l (EPA, 1977a)
  - Discharges of PCBs from manufacturers of PCBs, PCB capacitors, or PCB transformers - zero discharge (EPA, 1977a)

- Solid effluent stream - as stated earlier, no explicit emission levels are given, but it is inferred that the PCB Regulation applies to disposal of this stream. Thus, if the PCB content is below 50 ppm, disposal of incinerator solids is not regulated. If the content is above 50 ppm, disposal must be accomplished by Annex I incinerator, Annex II chemical waste landfill, or other approved methods.

Certain of the Annex I incinerator technical requirements, such as temperature; residence time; and stack gas O_2, CO, NO_x, and CO_2 are not pertinent to alternative disposal methods. Other requirements, such as control of HCl, total particulate matter, feed rate measurement, recordkeeping, storage, and contingency planning are pertinent. These are discussed in Chapter 7, which describes the approval process.

Because an alternative PCB destruction/disposal method must meet the requirements for either Annex I incinerators or high efficiency boilers, it is probable that most alternative methods will have to be tested for performance in a manner equivalent to a Trial Burn in order for approval to be obtained. It should be noted that tests in lieu of Trial Burns have been required of two high efficiency boilers (Hall-Enos and Zelenski, 1980; and Tennessee Eastman, 1979). Evaluations that should be performed during the approval process are described in Chapter 7.

2.1.2 Hazardous Waste Regulations

Interim final and final Hazardous Waste Regulations promulgated pursuant to RCRA indicate EPA's intention to incorporate the PCB Regulations into the Phase II Hazardous Waste Regulations (45 FR 33066). The subject of integration is being held in abeyance until Hazardous Waste Regulations are in place and operational. It seems probable that the Hazardous Waste Regulations will apply to PCB disposal operations, particularly those portions that establish standards for facilities and for permits for treatment, storage, and disposal facilities.

A significant feature of the Parts 265 and 265 of the Hazardous Waste Regulation are standards and interim status standards covering reprocessing. If an alternative method for PCBs is a reprocessing one and if the usable product contains less than 50 ppm of PCBs, then only the Hazardous Waste Regulations concerning transportation and storage need be followed (40 CFR 261.6).

2.1.3 Clean Water Act (CWA) Regulations

Regulations pursuant to the Clean Water Act, 40 CFR 129, set toxic pollutant effluent standards for PCBs. No discharge of PCBs is allowed (40 CFR 129.105) from manufacturers of: 1) PCBs, 2) electrical capacitors, and 3) electrical transformers. This standard applies to both new and existing sources. While 40 CFR 129.105 includes discharges from incineration areas in manufacturing plants, it does not appear that the standards mandated in 40 CFR 129.105 cover commercial contract incinerator operators because the definitions of manufacturers explicitly refer to those who: 1) produce PCBs, 2) produce or assemble capacitors in which PCBs are part of the dielectric, or 3) produce or assemble electrical transformers in which PCBs are part of the dielectric. Parts 116 and 117 of the Act define discharges under the Act, designate reportable quantities of PCBs spilled into waterways, and designate reporting requirements and fines.

The Clean Water Act also mandated preparation of a National Oil and Hazardous Substances Pollution Contingency Plan (40 CFR 1510). The final plan was published in 45 FR 17832. The Hazardous Waste Regulations also require the owner/operator of a hazardous waste facility to prepare a contingency plan (40 CFR 264.50) but states that the requirement can be met by appropriate amendments to an existing plan. The Electric Power Research Institute recently published two reports dealing with spill prevention, control, and countermeasures planning for PCBs for electric utility operators (EPRI 1979a, 1979b). EPA has published a manual for control of hazardous material spills (EPA 1977b).

2.1.4 Occupational Safety and Health Act Regulations

Under provisions of 29 CFR 1910.1, the OSHA 40-hour week limit for Aroclor 1242 is 1 mg/m^3 and 500 μg/m^3 for Aroclor 1254. In September 1977, the National Institute for Occupational Safety and Health recommended a time-weighted average for all PCBs of 1.0 $\mu g/m^3$. However, the OSHA standard has not yet been changed.

The current time-weighted average for PCBs as established by the American Conference of Governmental Industrial Hygienists is 1 mg/m^3 for Aroclor 1242 and 0.5 mg/m^3 for Aroclor 1254 (ACGIH, 1979).

2.1.5 Hazardous Materials Transportation Act Regulations

Under the Hazardous Materials Transportation Act, U.S. Department of Transportation (DOT) regulations in 49 CFR 171-177 cover the transport of hazardous waste materials. The rules place minor recordkeeping requirements on shippers and transporters of hazardous wastes and prohibit transportation and delivery to improper treatment, storage, or disposal sites. The Hazardous Waste Regulations in 40 CFR 263 set standards for transporters of hazardous wastes by adopting certain of the DOT regulations referenced above.

2.1.6 Public Notification and Participation

The PCB Regulations do not explicitly discuss public notification or participation in the approval process. It is not an unreasonable assumption, therefore, that it is the intent of the regulation that PCB disposal (thermal or alternative methods) facilities should be approved by Regional Administrators on their technical merit alone.

There is ample evidence of public concern about the operation and siting of hazardous waste disposal facilities. Local support for operation of such facilities is desirable if not essential. This section describes steps that can be taken to inform and promote public support. It also describes some public relations deficiencies to be avoided.

EPA's recently published proposed policy on public participation in Agency decision-making and rule making (45 CF 28911) offers guidance on ensuring public participation. EPA defined five basic tasks to be performed. These are briefly described below.

- Identification. Those groups or members of the public who may be interested in or affected by action (i.e., PCB destruction facility approval) should be identified. The responsible official must develop a contact list for each program or project.

- Outreach. Information about a PCB approval action must be conveyed to the public through mailings, personal communications, public service announcements, media briefings or ads, and other means. The information must include background, timetables, summaries of technical material, and, if possible, a description of social, economic, and environmental consequences.
- Dialog. The responsible official and interested or affected members of the public must be able to exchange views and explore issues. The dialog may take several forms; meetings, workshops, hearings, or correspondence. Timely dissemination of information is crucial.
- Assimilation. The results of the "outreach" and "dialog" tasks must be assimilated into the final decision, and the responsible official must demonstrate that he has understood and considered public concerns.
- Feedback. The responsible official must provide feedback to interested parties concerning the outcome of the public's participation. This feedback must state the action that was taken and indicate the effect that public participation had on the action.

Public concern caused considerable delays in performing a PCB Trial Burn in an industrial boiler at General Motors Corporation's Chevrolet plant in Bay City, Michigan. Zelenski et al., (1980) reported on deficiencies in the public participation process. The single major deficiency was that in the early stages the public was not provided with sound technical documentation showing that the PCB burn would be safe. Specific deficiencies were:

- The public was not informed of the proposed permit application in the early planning stages.
- Special interest groups were not informed of the proposed permit application in the early planning stages.
- Plant personnel were not informed in the early planning stages.
- Information needs of the public and special interest groups were not adequately anticipated.
- Information finally supplied was perceived as too technical.
- There was a lack of communication, coordination, and clearly defined responsibilities between participants in the permit approval process.

Zelenski, et al., (1980) made a number of recommendations, several of which are basically the same as may be required by EPA's proposed policy on public participation:

- Identify the concerned public and groups
- Communicate with the concerned public and groups
- Develop a relationship of cooperation with the public and groups
- Determine the level of support and incorporate that in plans for the proposed action

Consideration of the above public participation policy guidance should facilitate Agency permitting of alternative PCB disposal methods.

2.2 TECHNICAL FACTORS

2.2.1 Destruction Efficiency

The regulatory guidance presented in Section 2.1.1 identifies destruction efficiency as a necessary technical evaluation criterion for any alternative disposal method. An alternative method must "achieve a level of performance equivalent to Annex I incinerators or high efficiency boilers" (40 CFR 761.10(e)). Table 2 presents a summary of explicit or implied emissions limits for PCBs in the three generic process effluent streams from Annex I incinerators and high efficiency boilers.

2.2.2 Facility Design and Operation

When the PCB Regulations are incorporated into the Phase II Hazardous Waste Regulations, it is expected that facility standards (40 CFR 264, 265) will apply to PCB disposal facilities. Thus, a non-thermal PCB disposal process will have to be evaluated for compliance with Hazardous Waste Regulations requirements for waste receiving and storage areas, chemical analysis capability, inspection schedules, security, preparedness for and prevention of hazards, contingency plans, emergency procedures, manifest systems, and recordkeeping procedures.

2.2.3 Physical Form

It is anticipated that most alternate methods will be applied chiefly to PCB-contaminated liquids. However, some processes may be applicable to non-liquid PCBs or may be used *in situ* to decontaminate PCB Items, e.g., a

TABLE 2. EXPLICIT AND IMPLIED PCB EMISSION LIMITS FROM THERMAL DESTRUCTION PROCESSES

Method	Process Effluent Stream		
	Air	Liquid	Solid
Annex I Incinerator	1 mg/kg fed*	1.5 ng/l, 24-hr average [+] 6.2 μg/l, not to exceed [+]	50 ppm [#]
High Efficiency Boiler	<0.1% ** of PCB fed	ditto above	50 ppm [#]

[*] When burning non-liquid PCBs. Corresponds to a gas-phase destruction efficiency of 99.9999%. When burning liquid PCBs, performance is expected to be as good or better than when burning non-liquid PCBs

[+] EPA freshwater criterion (EPA 1978). Disposal of a scrubber effluent with a PCB concentration greater than 50 ppm is regulated by the PCB Regulation; disposal of a scrubber effluent with a PCB concentration less than 50 ppm is not. However, other regulations would govern discharge of such a stream from the site.

[#] Disposal of solid residues is assumed to be governed by the PCB Regulations: below 50 ppm disposal is not governed, above 50 ppm disposal is governed.

[**] No explicit values are given. Destruction efficiency is considered to be at least 99.9%. Total emissions should thus be less than 0.1 percent of PCBs input. Maximum PCB concentration in input feed is 500 ppm.

PCB Transformer. For a non-thermal process that is applied to non-liquids, the size of the solids may be a factor. Shredding and/or hammermilling may be necessary.

2.2.4 Range of Concentrations

The range of PCB concentrations that the alternate process can handle is important. A non-thermal process treating liquid containing greater than 500 ppm PCBs must be evaluated against Annex I incinerator requirements, while a non-thermal process treating liquid containing 50 to 500 ppm PCBs may be evaluated against high efficiency boiler requirements.

2.2.5 Special Process Requirements

Some alternate methods may require processing at high temperature and/or pressure, long residence time, etc., or have special requirements for storage, heat transfer, mass transfer, or materials of construction. Each of these engineering factors must be evaluated. The possibility of formation of toxic by-products must also be evaluated.

2.2.6 Restrictions on Composition

In some cases, thermal destruction of a PCB waste may be undesirable because it contains certain constituents (e.g., metals such as As or Hg) which might cause a hazard from the incinerator effluent streams. Similarly, a PCB waste may contain constituents which make non-thermal disposal disadvantageous, e.g., a catalyst poisoned by sulfur.

2.2.7 State of Technology

The non-thermal methods described in this report are not at commercial scale at this time and some have not been applied to PCB disposal. Thus, the state of the technological development of each non-thermal method is assessed and consideration is given to scale up, commercial potential, research potential, etc.

2.2.8 Test and Evaluation

It was noted in Section 2.1.1 that, because an alternative PCB disposal technique must meet the requirements of either Annex I incinerators or high efficiency boilers, it is expected that testing equivalent to a Trial Burn will be required. (The term "equivalent" is used in the sense that testing of emissions and destruction performance will be necessary. Not all of the Annex I incinerator or high efficiency boiler parameters are pertinent to alternative disposal methods.)

The facility operator should make sure to provide process instrumentation adequate to control and measure appropriate process parameters, such as PCB input rates, pressures, temperatures, effluent stream flow rates, etc. Appropriate test ports must be provided so that process stream samples may be acquired.

2.2.9 Scale-Up Implementation

As a non-thermal process is taken from the research, to bench scale, to pilot scale, to commercial scale stages of development, continuing engineering design and testing are necessary. For example, some of the chemical methods discussed in Chapter 3 generate heat during the reactions that destroy PCBs. Removal of excess heat is easy for small scale reactors but more difficult for large scale reactors. Testing for destruction efficiency is necessary to ensure that scale up has not reduced destruction efficiency.

2.3 ENVIRONMENTAL FACTORS

2.3.1 Impacts of Disposal Operation

Impacts of the overall disposal operation need to be assessed. This assessment logically occurs prior to implementing scale up of a process to commercial scale and thus is the responsibility of the developer of the method. In principal, any negative impacts should be more than offset by the advantages of having the disposal facility.

As part of evaluating a request for a waiver for an alternative process, the Regional Administrator needs to assess environmental impacts before he issues an approval. Subsequent paragraphs discuss criteria for assessing environmental impacts of various parts of an overall alternative disposal process.

2.3.2 Impacts of Process Effluents

A major factor in assessing potential environmental impacts of an alternative method is potential impacts of process effluent streams. Whether the alternative process is one of destruction, conversion, or reclamation, process effluent streams must be controlled, treated, disposed of, and/or sold. Not only residual PCB content, but also other possible constituents (e.g., toxic organics, leachable metals, biologicals, etc.) must be considered and dealt with in accordance with applicable regulations. Effects on air, water, and land should be assessed.

2.3.3 Potential Impacts of Accidents and Malfunctions

As noted in Section 2.1.2, the Hazardous Waste Regulations will require preparation of spill prevention, control, and countermeasures (SPCC) plans. Potential impacts of accidents at a non-thermal facility should be compared with the potential impacts of accidents at a thermal disposal facility. Thermal disposal facilities are required to have fail-safe process monitoring instrumentation that shuts off PCB feed when certain process parameters exceed pre-set limits. Similarly, a non-thermal disposal facility should be equipped with fail-safe devices and instrumentation for monitoring critical parameters.

2.3.4 Monitoring Programs

The Hazardous Waste Regulations will require routine inspection and monitoring activities to ensure that necessary maintenance activities occur and that PCBs and/or other potentially harmful substances do not migrate outside of the site boundaries. Evaluation of a commercial scale non-thermal disposal should thus consider materials of construction and architecture as these relate to maintenance. Process effluent containment, treatment, and disposal facilities should be evaluated with respect to prevention of escape of the streams from the site. Monitoring programs may include air monitoring, groundwater monitoring, and periodic physical examination of plant personnel (40 CFR 265, Subpart F).

2.3.5 Impacts of Transportation

In principal, the types of PCBs and PCB Items and transportation modes would be similar for both thermal and non-thermal disposal facilities. If there is a significant difference, then potential impacts of transportation should be evaluated. Regulations governing transportation of hazardous waste are found in 49 CFR Parts 171-179.

2.3.6 Closure and Post-Closure

The Hazardous Waste Regulations propose to require closure and post-closure plans. The technical aspects of such plans should be evaluated in context with 40 CFR 254, Subpart G.

2.4 ECONOMIC FACTORS

The PCB Regulations do not give EPA regulatory authority with respect to economic factors. Consequently, economic factors should have no bearing in an approval. However, a discussion of economic factors is included here out of general interest but not for regulatory purposes. Economic factors will play a significant role in the commercialization and operation of a PCB disposal facility, whether thermal or non-thermal. An uneconomic process, no matter how attractive technically, is not likely to be commercialized. The decision to commercialize a process obviously lies with the developer.

2.4.1 Capital Costs

Capital costs for facility construction or modification include costs of land, equipment, structural material, labor, pollution control equipment, process effluent treatment facilities, and money.

2.4.2 Operating Costs

Costs of labor, utilities, reagents, transportation, disposal, depreciation, etc. are components of operating costs. Operating costs in terms of cost per pound of waste and/or cost per pound of PCBs are important criteria in the decision to start and continue operations. If there is a saleable product resulting from a non-thermal disposal alternative, a reduction in operating costs results.

2.4.3 Disposal Costs

An important component of operating and capital costs is disposal of process wastes after necessary on-site treatment.

2.4.4 Credits for Products

Recycle/reclamation processes will produce potentially useful and saleable products. The resulting revenue reduces operating costs and makes process economics more attractive.

2.4.5 Closure and Post-Closure

Costs for closure and post-closure monitoring and maintenance must be assessed as part of overall process economics.

2.4.6 Regulatory Costs

Approval of an alternative PCB disposal facility may result in greater costs than for thermal disposal because of increased regulatory evaluation, testing, and notification requirements.

2.5 ENERGY FACTORS

2.5.1 Energy Debits

Thermal disposal facilities are purely destructive. Depending on the nature of the PCB waste to be destroyed, energy usage may range from low (high heat content waste) to high (low heat content waste). Incinerators generally blend a high heat content waste with a low heat content waste in order to reduce energy costs.

If a non-thermal process is operated primarily for PCB disposal, energy usage should be assessed in comparison with energy requirements for a thermal disposal facility of equal performance capability.

2.5.2 Energy Credits

If a non-thermal process produces a product that can be used for energy production or if some or all of the heat content of the waste stream is recovered, then an energy credit occurs. Heat recovery from hazardous waste incinerators is not practiced in the United States although the heat content of a PCB waste produces steam when it is burned in a high efficiency boiler. Recycle/resource recovery processes can be attractive with respect to energy credits. For example, a process that could economically remove/destroy the PCBs in mineral oil dielectric fluid would lead to the saving of millions of gallons of oil that would otherwise be incinerated.

3. A REVIEW OF POTENTIAL NON-THERMAL DISPOSAL METHODS

3.1 PHYSICOCHEMICAL METHODS

This section of the report describes current research and development of various physicochemical disposal methods for PCBs and PCB related materials. None of these processes are "state-of-the-art". Most exist only on the laboratory scale with limited data available. Many of the assumptions must be qualitative in nature. Technical information gaps are widespread in the literature, thus making it very difficult to present analytical data.

Specific processes covered may apply to the treatment of PCB Transformer fluids containing >500 ppm PCBs, capacitors, other heat transfer fluids or PCB Articles containing more than 50 ppm PCBs. Certain processes covered may apply to aqueous systems only, while others may not have been applied to PCB degradation or detoxification at all. These latter processes will be described in this section and evaluated in the next section based on the possibility of these processes being able to be adapted to PCB treatment.

3.1.1 Adsorption Processes

An extremely useful method for removing chlorinated hydrocarbons from aqueous waste streams is to contact the stream with activated carbon by passing it through a vessel filled with a carbon slurry or with carbon granules. Impurities from the aqueous streams are removed by adsorption onto the charcoal. The complete adsorption system usually consists of a few columns used as contactors connected to a regeneration system, as shown in Figure 2. After a certain period of time, the carbon adsorptive capability is exceeded, and the carbon must be regenerated. Fresh carbon is periodically added to the system to replace that lost during regeneration and transport. A multiple hearth furnace is included in the regeneration system (Hansen and Rishel, 1979). Activated carbon has an affinity for organics, and its use for organic

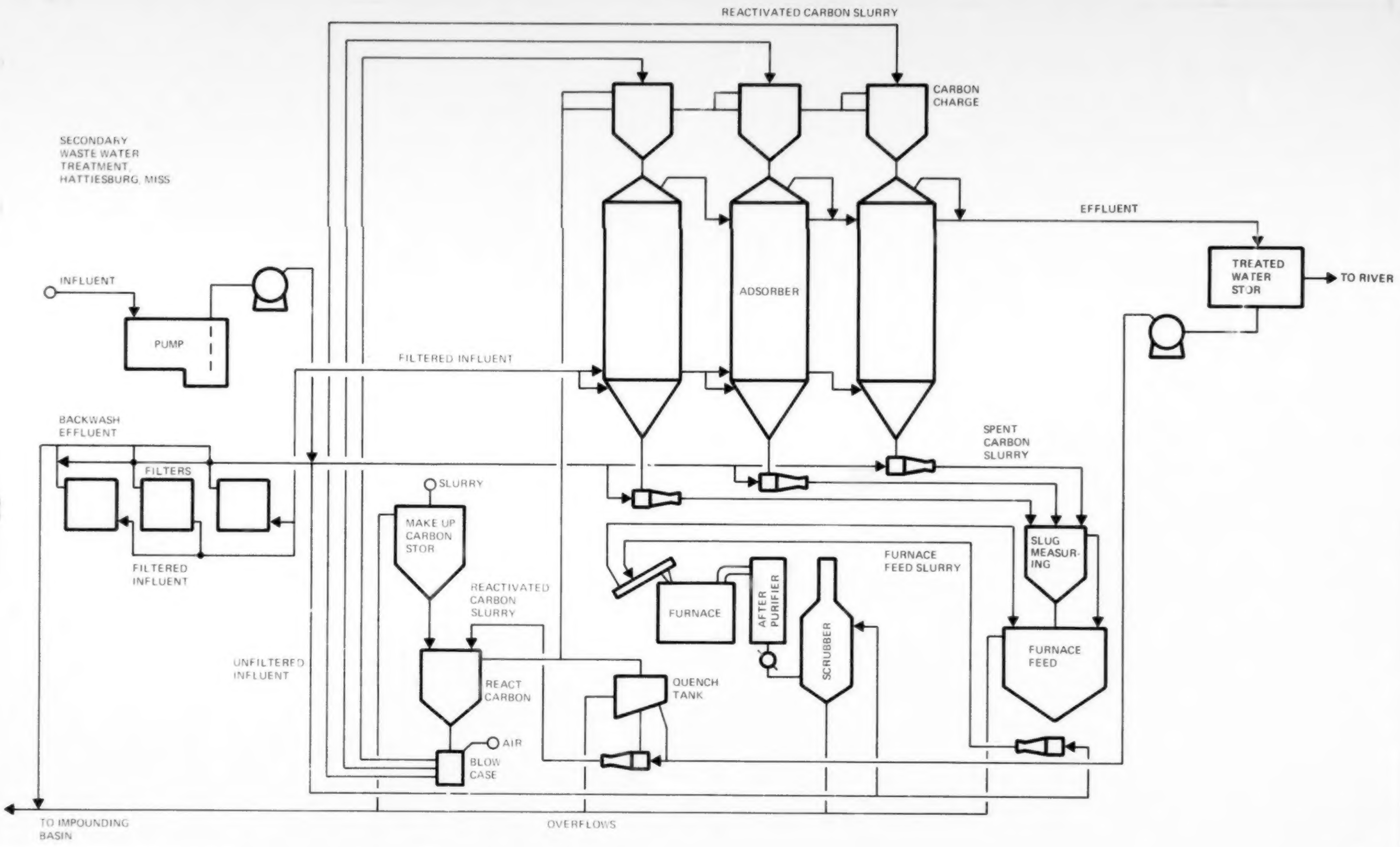

REACTIVATED CARBON SLURRY
CARBON CHARGE
SECONDARY WASTE WATER TREATMENT, HATTIESBURG, MISS
EFFLUENT
INFLUENT
ADSORBER
TREATED WATER STOR
TO RIVER
PUMP
FILTERED INFLUENT
BACKWASH EFFLUENT
SPENT CARBON SLURRY
FILTERS
SLURRY
MAKE UP CARBON STOR
SLUG MEASUR-ING
FURNACE FEED SLURRY
FILTERED INFLUENT
REACTIVATED CARBON SLURRY
FURNACE
AFTER PURIFIER
SCRUBBER
FURNACE FEED
UNFILTERED INFLUENT
REACT CARBON
QUENCH TANK
AIR
BLOW CASE
TO IMPOUNDING BASIN
OVERFLOWS

Figure 2. Schematic diagram of a generalized carbon adsorption system incorporating thermal regeneration of the carbon (Hanson and Rishel, 1978).

contaminant removal from wastewater is common. It is estimated that there are over 100 large scale systems currently in use for industrial and municipal wastewater treatment (Zanitsch, 1978). Carbon adsorption is particularly favorable when the solutes have a high molecular weight and low water solubility, as is the case with dissolved PCBs. Carbon adsorption was one of the most promising water treatment systems for removing dissolved PCBs, as indicated in a study done by Versar Inc. in 1976 (Versar Inc., 1976). It was found in that study that the activated carbon system was capable of reducing the concentration of PCBs in the aqueous effluent to less than 1 ppb (Versar, Inc., 1976).

In 1976, the General Electric Capacitor Products Department installed a system to eliminate the discharge of PCBs to the Hudson River from the Hudson Falls and Fort Edward manufacturing sites. All wastewater discharged from the site was treated by carbon adsorption before the discharge to the river. This adsorption process worked extremely well for dilute aqueous streams contaminated with PCBs (Arisman, 1979). It was found that, while the carbon treatment system could reduce the concentration of PCBs in the aqueous effluent to less than 1 ppb, it was not a very cost effective method. This, coupled with carbon disposal or regeneration requirements, provided a basis for the EPA and the General Electric Capacitor Products Department to investigate alternate treatment systems, i.e., UV-Ozonation and catalytic reduction.

Application of activated carbon adsorption processes is less common to non-aqueous streams than to aqueous streams. However, the U.S. Air Force (U.S. Air Force, 1976) funded studies on using activated carbon to remove a contaminant (2,3,7,8-tetrachlorodibenzo-p-dioxin, TCDD) with an average concentration of 2 ppm from Herbicide Orange, a nominally 50:50 mixture by volume of n-butyl esters of 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid. TCDD was reduced to 0.1 ppm or less, and the process was considered technically and economically feasible. However, the U.S. Air Force concluded that the technology to dispose of the TCDD-contaminated activated charcoal (approximately 640 tons of charcoal) did not exist, and the Herbicide Orange stocks were instead successfully incinerated at sea (Ackerman, et al., 1978).

From a technical point of view, adsorption processes for removing organic compounds from liquid streams are attractive because they offer the possibility of resource recovery, e.g., removal of PCBs from mineral oil dielectric fluid. Adsorption processes are not destructive. They merely reduce the contaminant concentration in the liquid stream and concentrate the contaminant in the adsorbent. To be economical, the contaminant must be removed from the adsorbent, so that an adsorption process applied to PCB disposal must be coupled with a second disposal/destruction process to handle PCBs removed from the adsorbent during regeneration.

3.1.2 Catalytic Dehydrochlorination

Catalytic dehydrochlorination is based on the reaction of polychlorinated hydrocarbons with high pressure hydrogen gas in the presence of a catalyst (La Pierre, et al., 1977). The reaction is:

$$RCl_n + xH_2 \xrightarrow[\Delta]{\text{Catalyst}} RH\,x\,Cl_{n-x} + xHCl$$

where n and x are small integers.

The reasoning behind this reaction is that partially dechlorinated or nonchlorinated compounds could be less toxic and, therefore, could be biodegraded more easily than highly chlorinated compounds. This process has been directly applied to the detoxification of PCBs. A flow diagram of the hydrodechlorination process is presented in Figure 3. This process is adapted for batch operation and has been done on bench scale only.

The PCBs are batch fed into a rotary extractor. The extraction uses hot ethanol, and the extracted material is pumped to a reaction vessel. Sodium hydroxide in ethanol is added next to react with liberated HCl gas which could deactivate the catalyst and could cause corrosion problems. The reaction vessel is kept under a pressure of 3 to 5 MPa (30 to 50 atm.) with H_2 gas.

The catalyst can be either 61 percent nickel on kieselguhr or 10 percent palladium on charcoal. The catalyst should be prereduced in hydrogen at 643°K (1157°F) for best results. During reactor vessel discharging,

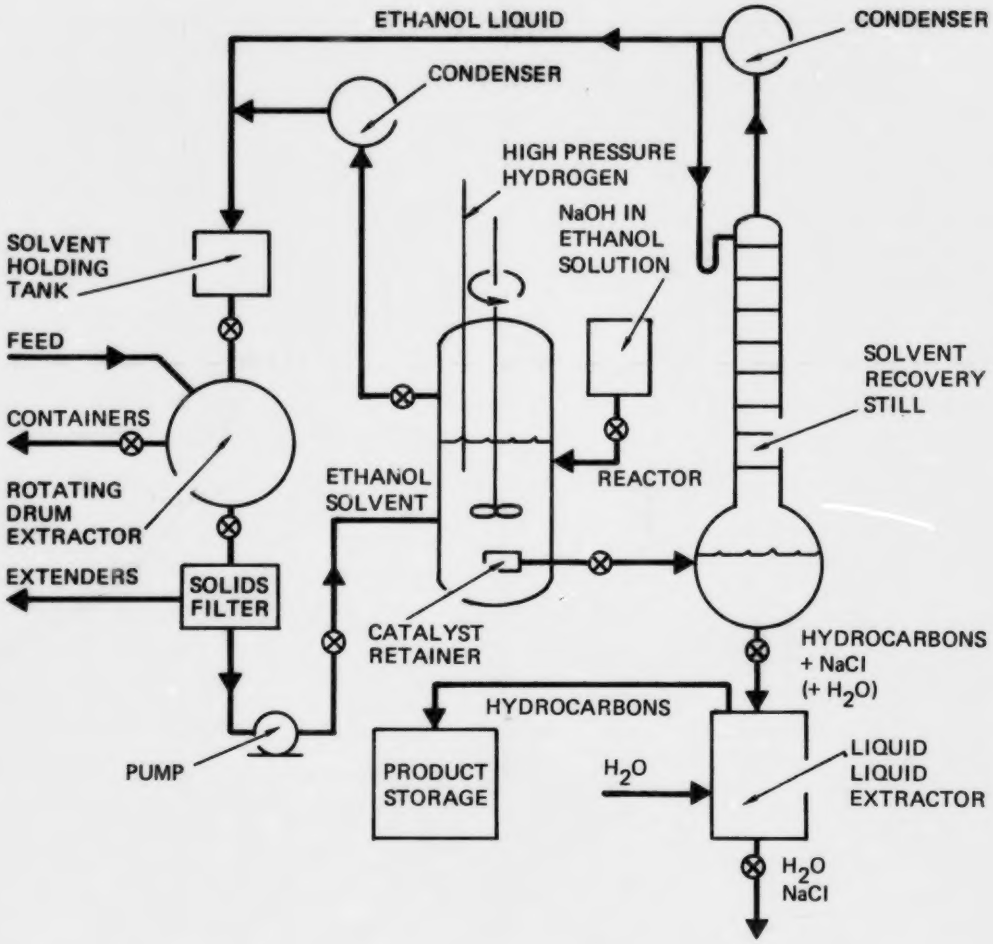

ETHANOL LIQUID
CONDENSER
CONDENSER
HIGH PRESSURE HYDROGEN
NaOH IN ETHANOL SOLUTION
SOLVENT HOLDING TANK
FEED
CONTAINERS
SOLVENT RECOVERY STILL
ROTATING DRUM EXTRACTOR
ETHANOL SOLVENT
REACTOR
EXTENDERS
SOLIDS FILTER
CATALYST RETAINER
HYDROCARBONS + NaCl (+ H_2O)
HYDROCARBONS
PRODUCT STORAGE
H_2O
LIQUID LIQUID EXTRACTOR
PUMP
H_2O NaCl

Figure 3. Schematic flow diagram for hydrodechlorination process (Kranich, et al., 1977).

catalyst particles of 0.15 to 0.30 cm diameter are retained on a stainless steel screen. The quantity of catalyst should be 0.2 percent of the weight of the PCBs to be dechlorinated.

Experimentally determined reaction conditions for pressure and temperature are 3 to 5 MPa (30 to 50 atm) and 373 to 393°K (671 to 707°F). Reaction time depends on the desired degree of dechlorination for a specific compound. According to Figure 4, about 90 percent of the chlorine may be removed from PCBs in about 5 hours (Kranich, et al., 1977). Completion of the reaction is determined by a decreasing demand for sodium hydroxide. After completion, the reaction mixture is pumped to a solvent recovery still. The catalyst particles are retained on a stainless steel screen in the reactor vessel. Ethanol is then distilled through a bubble cap column or another type of fractionating head and returned to the solvent holding tank. The products consisting of hydrocarbons, incompletely dechlorinated materials, salt, and water are washed with water in a liquid-liquid extraction vessel. The hydrocarbon materials are stored for possible usage, and the salt water is discarded.

Since this process has not been scaled up, industrial data are not available.

3.1.3 Chlorinolysis (Chlorolysis)

Chlorinolysis is an emerging process for the conversion of chlorinated hydrocarbons. This is a vapor phase reaction in which chlorine is added to the waste material under high pressure and low temperature or high temperature and low pressure. A catalyst is not used in the process (S.S.M., 1974). If the waste consists of only carbon and chlorine atoms, the product will be carbon tetrachloride. If the waste contains oxygen or hydrogen, carbonyl chloride and hydrogen chloride are also produced (S.S.M., 1974). Because of corrosion and oxidation, the reactor must be composed of special materials.

Chlorination as a method of disposing of hazardous wastes was first suggested in 1974 (Anon., 1974). Exhaustive chlorination can be accomplished over a wide range of pressures and temperatures. Farbweke Hoeschst AG, Frankfurt/Main, Germany, has developed a process where hydrocarbons and their chlorinated derivatives are completely converted to carbon tetrachloride and

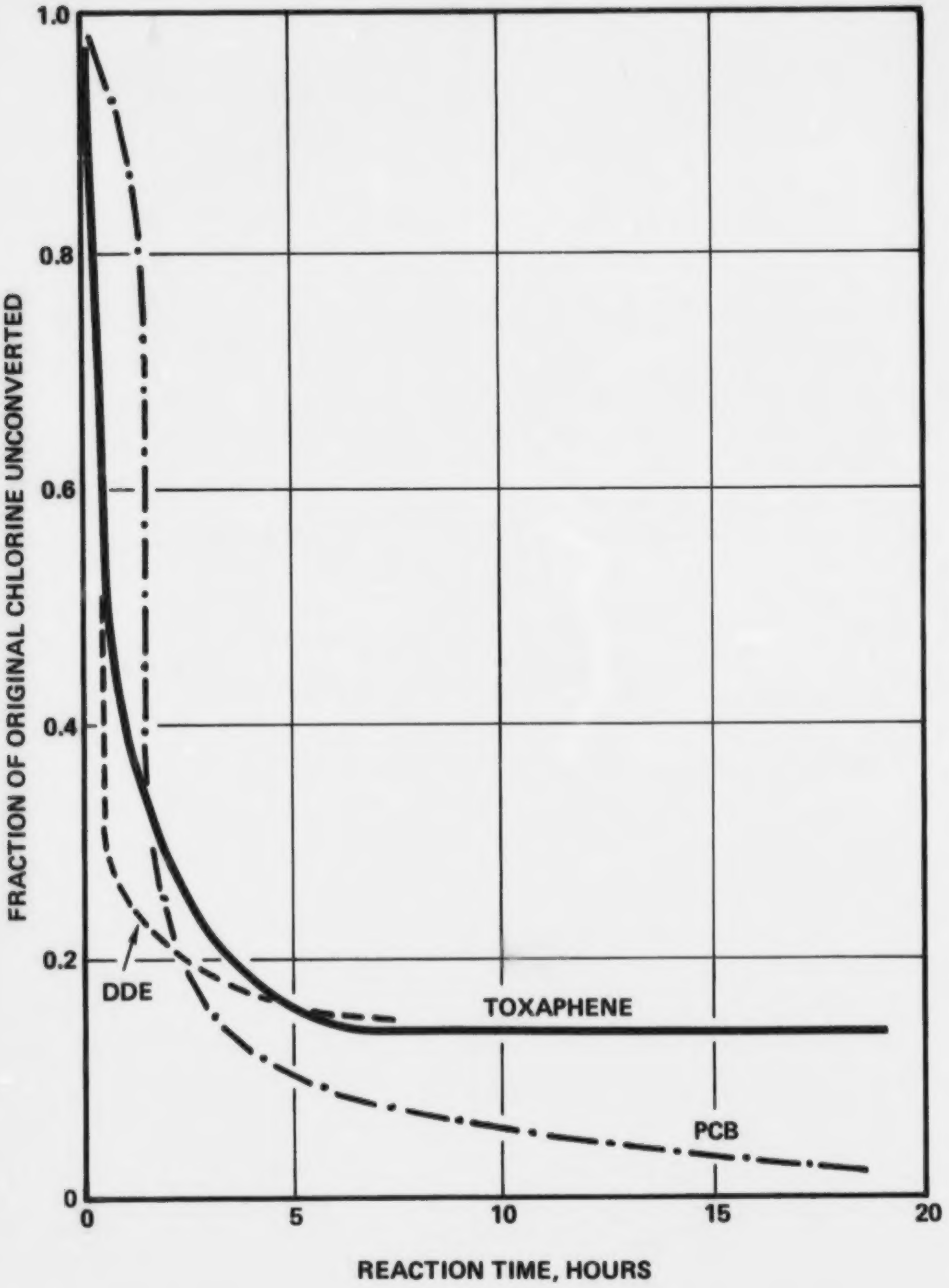


Figure 4. Experimental reaction process for three chlorinated hazardous materials (Kranich, et al., 1977).

hydrogen chloride at pressures up to 24 MPa (240 atm) and temperatures up to 893°K (1575°F) (Krekeler et al., 1975). Figure 5 presents a flow diagram of the Hoeschst AG chlorolysis process. Although it is not documented if chlorolysis on PCBs has been accomplished, reaction products would be CCl_4 and HCl. Organic wastes that contain sulfur, nitrogen, or phosphorous may have ill effects on the process. For example, if sulfur in excess of 25 ppm is contained in the feedstream, severe corrosion of the nickel tube catalytic reactor could occur.

An extensive literature search indicates that the Hoechst Uhde process is the only one that has some capability of handling aromatic hydrocarbon feedstocks. The Hoechst Uhde process is the only chlorolysis process that does not produce organochlorine residues in large quantities since all wastes initially produced can be recycled for further degradation. A demonstration plant producing 8,000 metric tons/year of carbon tetrachloride has been on stream in Frankfurt, Germany, since November 1970. A commercial plant producing 50,000 metric tons/year of carbon tetrachloride has been on stream at the same location since 1977.

The chlorolysis plant consists of a pretreatment section for the treatment of all the wastes entering the unit, a reactor section where the heated residues are converted into HCl and CCl_4, a distillation section for the separation of reaction products, and an incineration section for the disposal of remaining residues. An adsorption unit is used for the elimination of waste gases containing Cl_2 gas and HCl.

3.1.4 The Goodyear Process

The Goodyear Tire and Rubber Company has recently developed a process (Goodyear, 1980) to degrade low levels of PCBs. Two allied approaches showed favorable results: the catalytic hydrogenolysis of carbon-chlorine bonds over a palladium catalyst and the cleavage of carbon-chlorine bonds by the use of sodium or organo-sodium reagents. Both of these methods were shown in Goodyear's laboratories to dehalogenate PCB materials from levels of 120 ppm to less than 10 ppm. The reaction with sodium or organo-sodium was found to operate at lower temperatures and, therefore, was chosen as the preferred process.

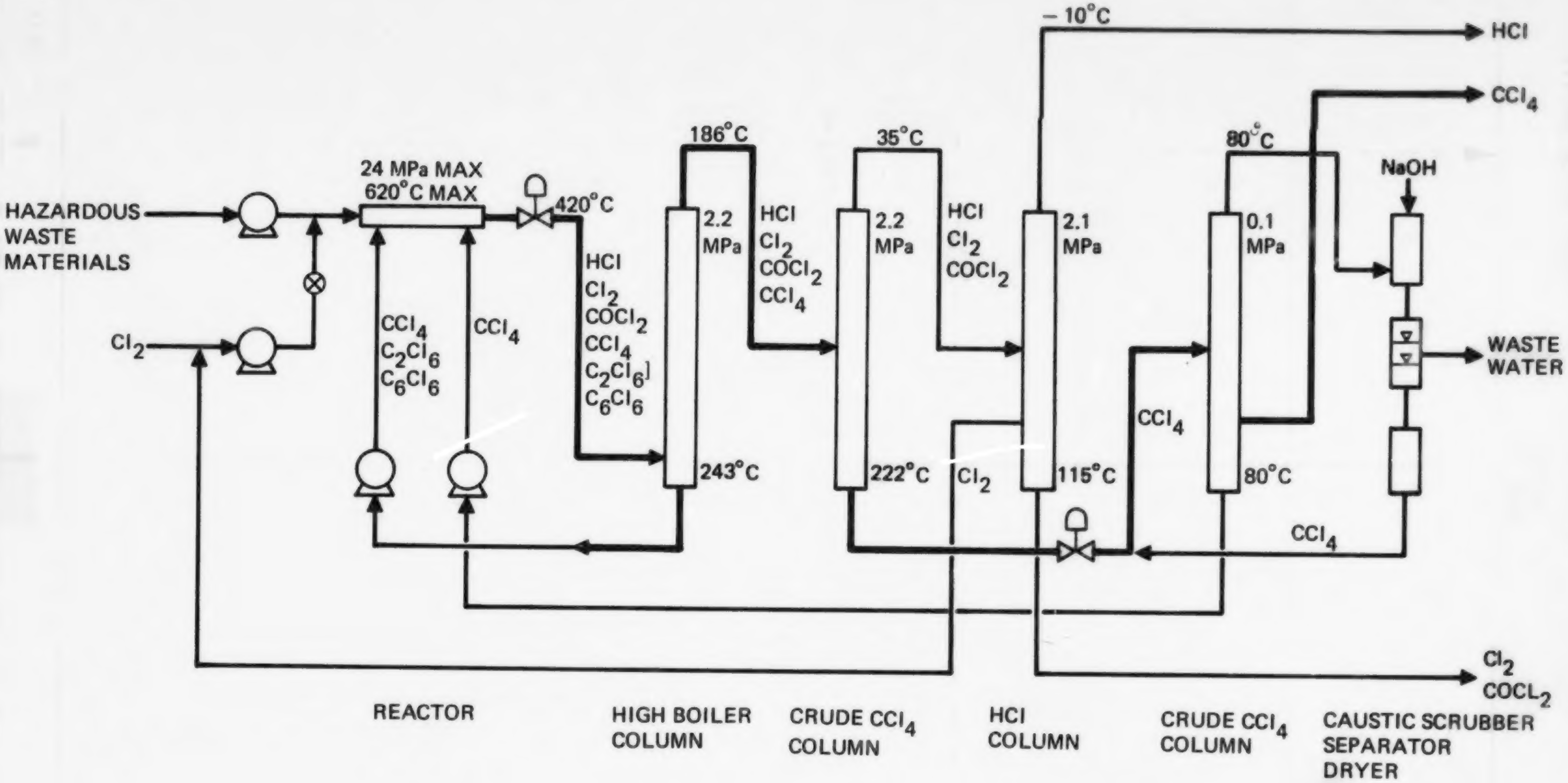

HAZARDOUS WASTE MATERIALS
Cl_2
24 MPa MAX
620°C MAX
420°C
HCl
Cl_2
$COCl_2$
CCl_4
C_2Cl_6
C_6Cl_6
CCl_4
C_2Cl_6
C_6Cl_6
CCl_4
186°C
2.2 MPa
243°C
HCl
Cl_2
$COCl_2$
CCl_4
35°C
2.2 MPa
222°C
HCl
Cl_2
$COCl_2$
Cl_2
− 10°C
2.1 MPa
115°C
CCl_4
80°C
0.1 MPa
80°C
CCl_4
NaOH
HCl
CCl_4
WASTE WATER
Cl_2
$COCl_2$
REACTOR
HIGH BOILER COLUMN
CRUDE CCl_4 COLUMN
HCl COLUMN
CRUDE CCl_4 COLUMN
CAUSTIC SCRUBBER
SEPARATOR
DRYER

Figure 5. Schematic diagram of the Hoechst AG Chlorolysis process (Krekeler, et al., 1975).

The reactions were found to be extremely fast at ambient temperature. Recently, Japanese researchers have successfully dechlorinated high concentrations of PCBs in tetrahydrofuran at 273°K (Oku, Yasufuku and Kataoka, 1978). They claim that only 1.1 to 1.3 moles of sodium naphthalide per mole of chlorine (as Cl) was needed to remove all the organic chlorine. A similar method was also researched at the University of Waterloo, Canada (Electronic and Engineering Times, 1979). The Goodyear research team attempted to adapt the Japanese methods to the removal of low level (ppm) PCB contamination. It was soon discovered that 1.1 to 1.3 molar ratios of sodium naphthalide to chlorine were too low to obtain any meaningful reduction in PCB levels. As shown in Figure 6, a 50-100 mole ratio was found to be the minimum necessary to remove 98 percent of the PCBs from the heat transfer oil composed of 83 ppm PCB. This reaction was found to proceed in less than five minutes under an inert atmosphere. Due to procedural difficulties with the preparation of the sodium naphthalide reagent, a new procedure for reagent preparation was developed. 150-400 ml of either fresh or contaminated heat-transfer fluid per gram-atom of sodium was used to form an extremely reactive form of sodium containing a low surface oxide coating. This was done by heating pieces of sodium in the heat-transfer fluid under an inert atmosphere to 423-443°K for 5-10 minutes with rapid stirring. This solution was then cooled to ambient temperature while stirring. The sodium droplets solidified into bright spheres. The reagent itself was next formed by the addition of the tetrahydrofuran-naphthalene solution to the sodium in the heat-transfer fluid at ambient temperature. The reagent was completely formed after one hour with gentle stirring. This method of reagent preparation was found to work very effectively on both small and very large scales. The reagent could next be added to a large amount of additional heat-transfer fluid. The amount of reagent would be adjusted to give a minimum reagent/chlorine ratio of 50 to 100. This reaction occurred rapidly at room temperature. After about one hour, the excess reagent was quenched by adding at least a stoichiometric quantity of water. This quenched fluid was next stripped under vacuum to recover tetrahydrofuran and naphthalene for possible recycling. The residue was vacuum distilled again. The recovery heat-transfer fluid contained less than 1 ppm PCB. The recovered heat-transfer fluid contained less than

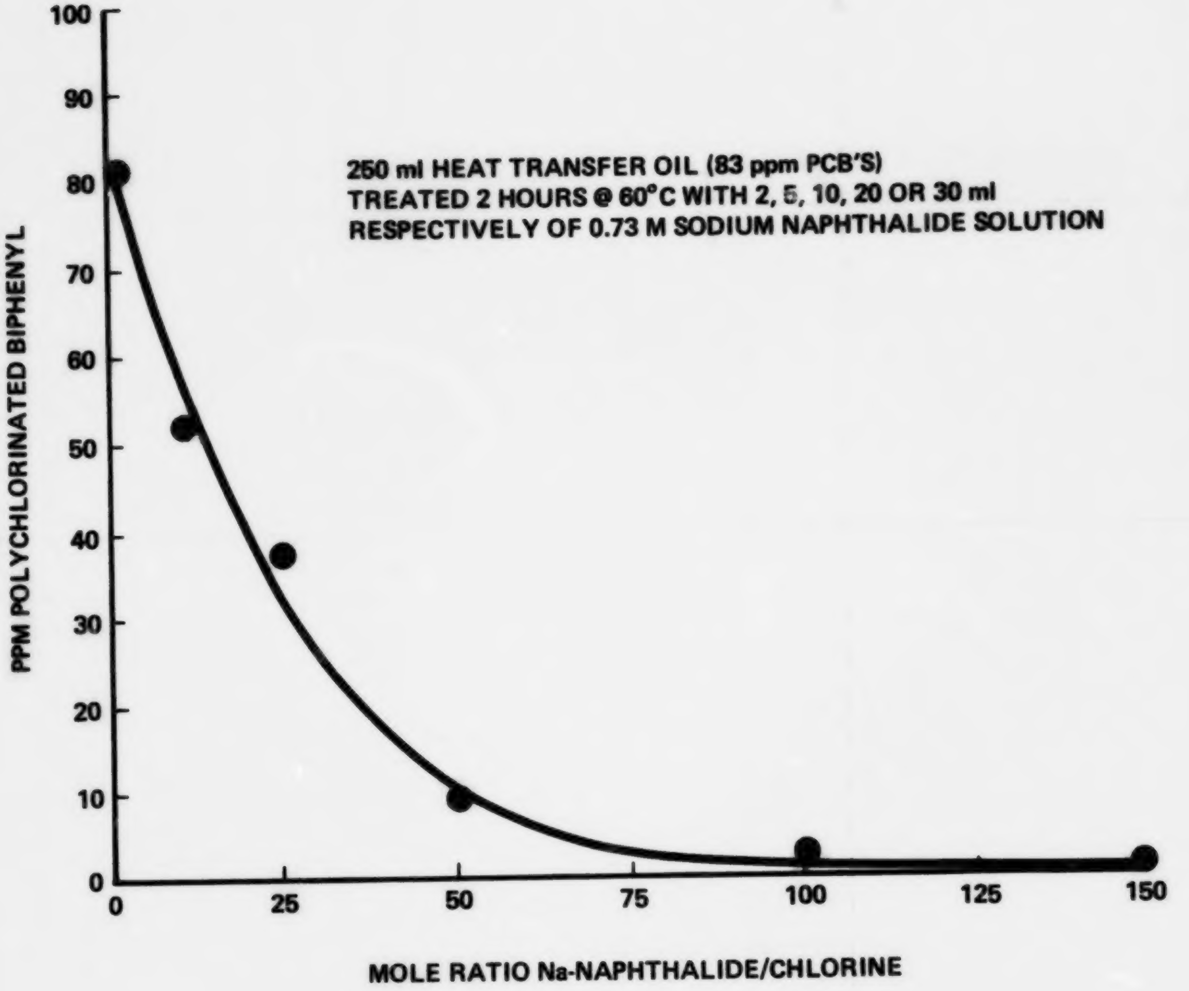


Figure 6. Amount of reagent versus PCB concentration used in Goodyear process (Goodyear Tire and Rubber Company, 1980).

1 ppm PCB. The residues in the pot from the second distillation contained non-halogenated polyphenyls, which could be safely burned, and sodium chloride.

This process has been adapted for use on a commercial scale. Material containing 130 ppm PCBs have been reduced to less than 10 ppm. Figure 7 represents a schematic of the Goodyear Process.

3.1.5 Microwave Plasma Destruction of PCBs

Lockheed Missiles and Space Company, Palo Alto Research Laboratory (LPARL), has developed a process to detoxify PCBs and other hazardous materials based on microwave plasma destruction (Oberacker and Lees, 1977). Research started on the bench scale and has been expanded to a unit which can successfully detoxify PCBs at the rate of 0.45 to 3.2 kg/hr (1 to 7 lb/hr). EPA has sponsored a project to demonstrate a 4.5 to 13.5 kg/hr (10 to 30 lb/hr) apparatus. A future goal is to develop a 40 to 50 kg/hr (~100 lb/hr) version.

Figures 8 and 9 are schematic diagrams of the microwave plasma unit. The unit was built from commercially available standard glass apparatus and electronic hardware. Two 2.5 kW power transformers provide energy at 2450 MHz to the microwave reactor. This energy is fed through wave guides and "focused" just before entering the applicator assembly surrounding the quartz reaction tube.

A continuous sampling gas analyzer was placed in line between the reactor tube outlet and the ice water cold trap to monitor the detoxification process. An infrared spectrophotometer and a gas chromatograph were also used for monitoring.

The PCB material was added to the system as a pure liquid. Operating pressure was 1.3 to 13.3 kPa (10 to 100 torr). Samples of PCB material to be detoxified were introduced through a dropping funnel. The carrier gas was fed above the dropping funnel. The PCB material was transported by both gravity and by the carrier gas (oxygen, oxygen-argon, or steam) through a quartz reaction tube. The reaction products were contained in traps cooled with ice water or liquid nitrogen placed between the reaction tube and the vacuum pump.

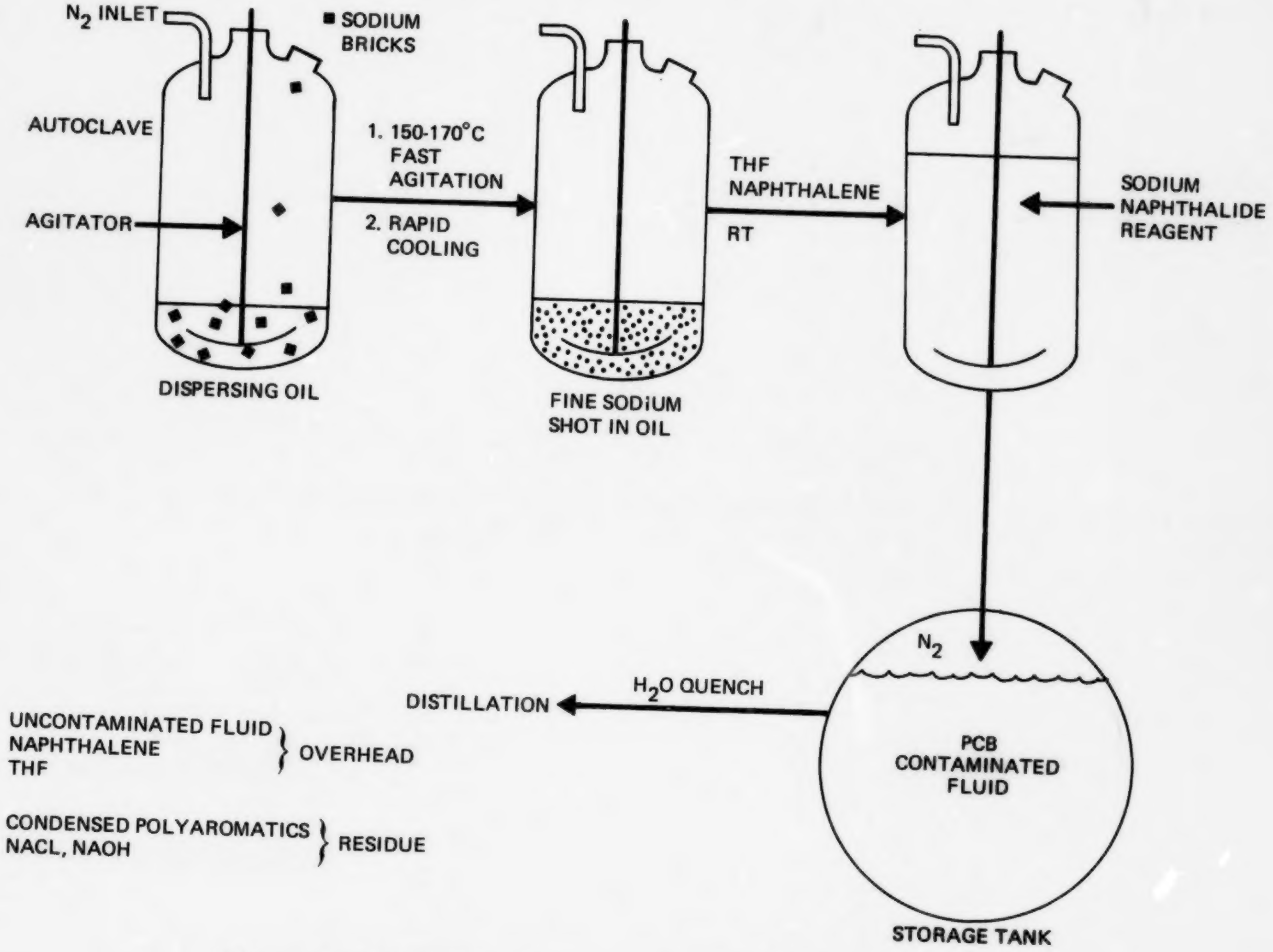

N2 INLET
■ SODIUM BRICKS
AUTOCLAVE
AGITATOR
DISPERSING OIL
1. 150-170°C FAST AGITATION
2. RAPID COOLING
FINE SODIUM SHOT IN OIL
THF NAPHTHALENE
RT
SODIUM NAPHTHALIDE REAGENT
N2
PCB CONTAMINATED FLUID
STORAGE TANK
H2O QUENCH
DISTILLATION
UNCONTAMINATED FLUID
NAPHTHALENE
THF
OVERHEAD
CONDENSED POLYAROMATICS
NACL, NAOH
RESIDUE

Figure 7. Schematic of Goodyear process (Goodyear Tire and Rubber Company, 1980).

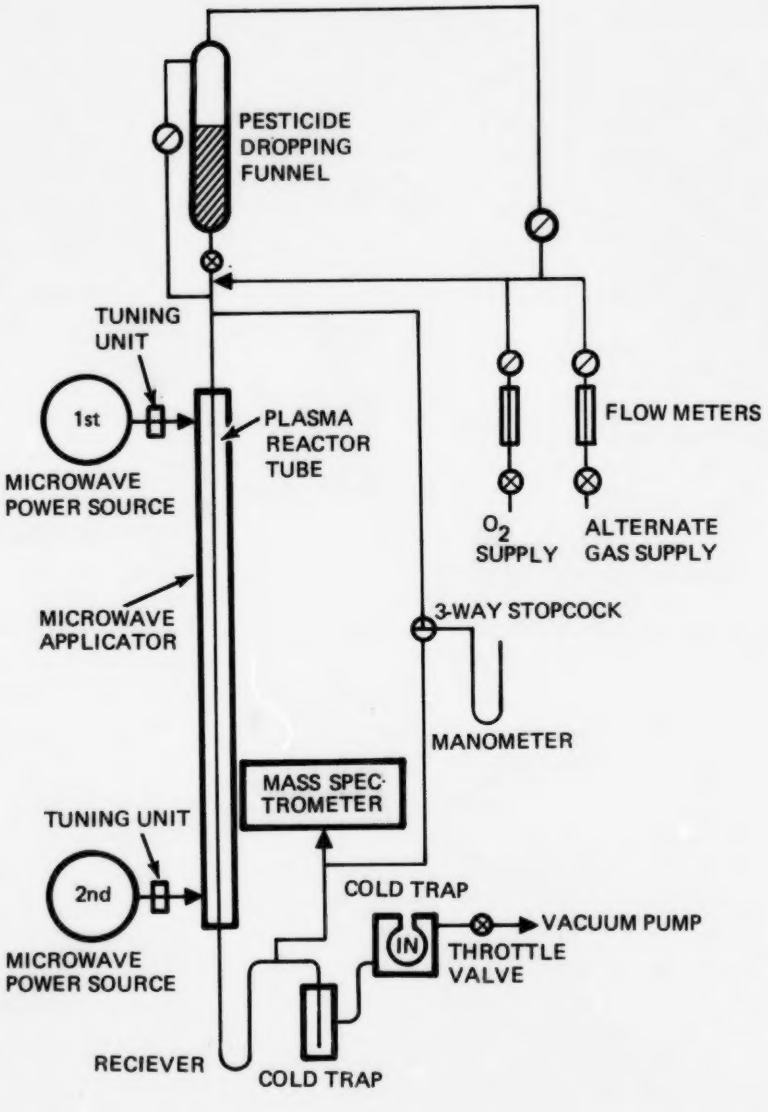

PESTICIDE
DROPPING
FUNNEL
TUNING
UNIT
1st
PLASMA
REACTOR
TUBE
MICROWAVE
POWER SOURCE
FLOW METERS
O_2
SUPPLY
ALTERNATE
GAS SUPPLY
MICROWAVE
APPLICATOR
3-WAY STOPCOCK
MANOMETER
MASS SPEC-
TROMETER
TUNING UNIT
2nd
COLD TRAP
VACUUM PUMP
IN
THROTTLE
VALVE
MICROWAVE
POWER SOURCE
RECIEVER
COLD TRAP

Figure 8. Schematic of microwave plasma system (Bailin and Hertzler, 1976).

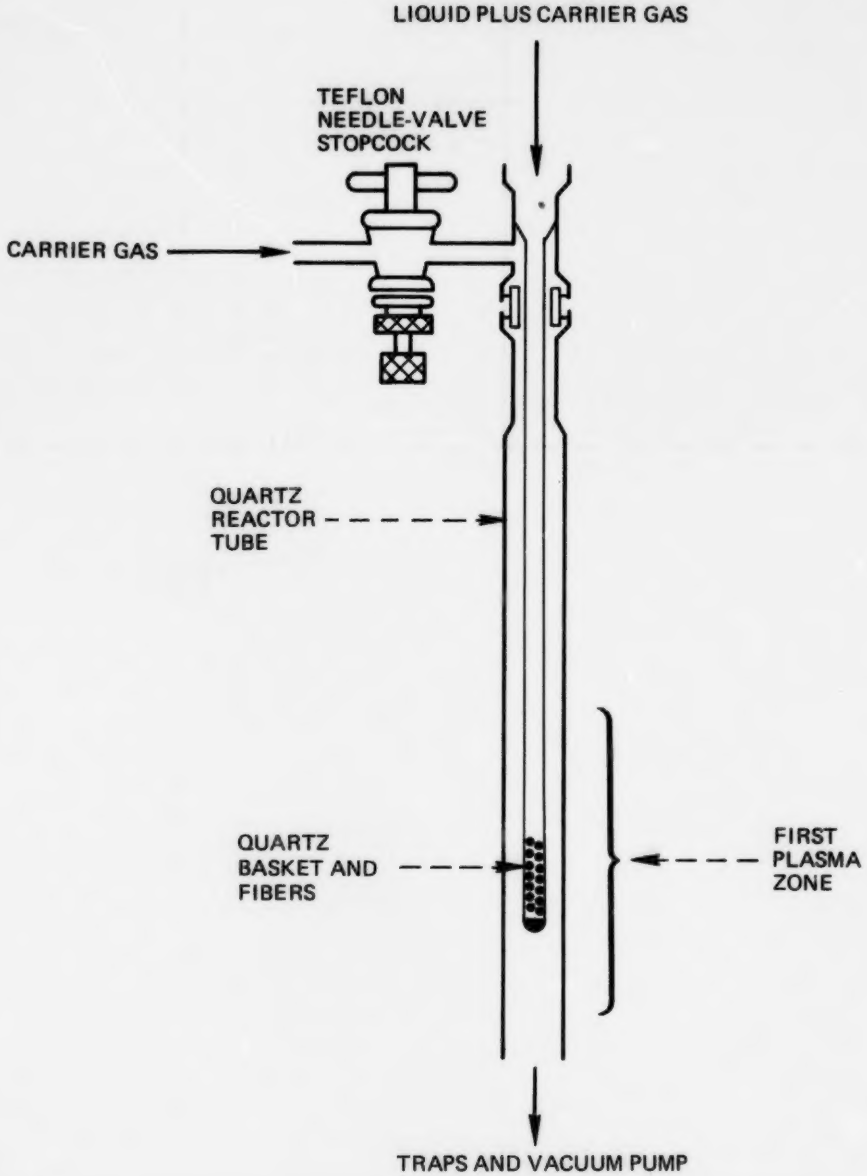

LIQUID PLUS CARRIER GAS
TEFLON NEEDLE-VALVE STOPCOCK
CARRIER GAS
QUARTZ REACTOR TUBE
QUARTZ BASKET AND FIBERS
FIRST PLASMA ZONE
TRAPS AND VACUUM PUMP

Figure 9. Quartz mesh basket within microwave plasma reactor (Bailin and Hertzler, 1976).

The PCB material is destroyed in the reaction tube by applying the microwave radiation. This generates an ionized carrier gas. The microwave induced plasma reacts with the neutral organic PCB molecules to form free radicals which then either dissociate or react with oxygen to form simple reaction products such as SO_2, CO_2, CO, H_2O, $COCl_2$, etc. The discharge is usually ignited with a Tesla coil.

After the PCB material is destroyed, the reaction products which are now vapors and any other condensible material are sent into an ice water bath and then to a liquid nitrogen cold trap. The carrier gas then enters the vacuum pump.

The PCBs used were of the Aroclor 1242 variety. Feed rates were from 0.18 to 0.5 kg/hr. Residence times varied from 0.5 to 1 sec. The results and operating variables are summarized in Table 3.

The most recent microwave plasma detoxification studies are dealing with the scale up of this process (Hertzler, et al., 1979). An expanded volume, 5-kW system was constructed with a throughput of 2 to 11 kg/hr.

3.1.6 Ozonation Processes

Ultraviolet (UV)-ozonolysis is a process that destroys or detoxifies hazardous chemicals in aqueous solution utilizing a combination of ozone and UV irradiation. Fairly simple equipment is required on the laboratory scale: a reaction vessel, an ozone generator, a gas diffuser or sparger, a mixer, and a high mercury vapor lamp (Wilkinson, et al., 1978).

TABLE 3. SUMMARY OF MICROWAVE OXYGEN PLASMA REACTIONS

PCB	Microwave Power, kW	Feed Rate kg/hr	Pressure Pa (torr)	Oxygen Gas Flow 1/hr	Reactor Packing	Conversion (%)
Aroclor 1242	4.6	0.27	2300-4700 (17-35)	323	Wool plug	99
Aroclor 1242	4.2	0.5	2500-4800 (19-36)	395	Wool plug	99
Aroclor 1254	4.5	0.18	1700-3300 (13-25)	360	Solid quartz rings	99

Sources: Bailin and Hertzler (1976) and Bailin (1977).

The hazardous material in aqueous solution is placed in a plastic or steel reactor fitted with a gas diffuser or sparger at the bottom. A temperature sensing device, an electrode for monitoring pH, and a mixer or impeller are contained with the reactor. A high pressure mercury lamp is placed inside the solution to provide a source for UV radiation. Ozone is generated by electrical discharge. Excess ozone is vented out through a potassium iodide trap.

Process development and demonstration of UV-ozonation of dilute aqueous streams contaminated with various PCB levels was carried out by Westgate Research Corporation under contract to General Electric Corporation (Arisman, 1979). This technology is still in the research stage, but it has been shown to be effective on the bench scale in destroying PCBs and degrading the products to CO_2, HCl, and H_2O (Versar Inc., 1976). The bench scale experiments used a 36" x 6" cylindrical reactor. Ozone and oxygen were diffused from the bottom of the reactor through porous ceramic spheres. Ozone concentrations were 2-3 percent in O_2. The total O_2 mass flow rate varied from 35 to 120 ng/min. A volume of 11 liters of PCB-contaminated water was treated per batch. Reaction times varied from 1-2 hours. PCB concentrations ranged from 20-50 ppb. Important variables effecting the reaction are: O_3 mass flow rate, O_3 concentration, UV intensity, and residence time. The results of these bench tests gave approximate information about UV-ozone reactor sizing, ozone generator output requirements, and the effect of UV light on the rate of oxidation (Arisman, 1979). This UV-ozonation process applies only to dilute aqueous streams and not to non-aqueous fluids containing high concentrations of PCBs. Figure 10 depicts basic apparatus needed for ozonation.

3.1.7 Photolytic Processes

Ultraviolet radiation may drive chemical reactions in many chlorinated hydrocarbons under controlled laboratory conditions (Mitchell, 1961). Much research has been done on the photodecomposition of various classes of pesticides by using UV light (Crosby and lee, 1969; Plimmer, 1970, 1972, 1977; and Rosen, 1971). The photodecomposition of PCB is now being studied in the laboratory to determine the structure of the resulting products and the

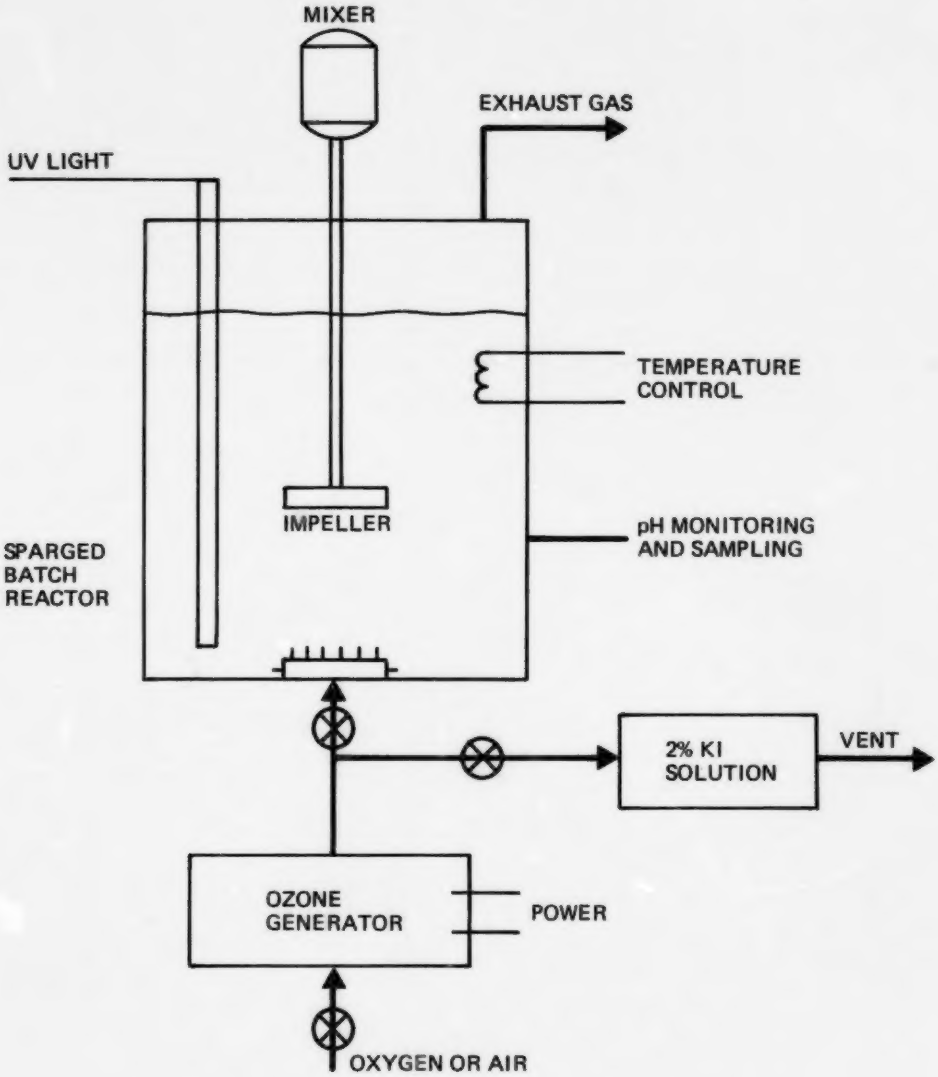

MIXER
EXHAUST GAS
UV LIGHT
TEMPERATURE CONTROL
IMPELLER
pH MONITORING AND SAMPLING
SPARGED BATCH REACTOR
2% KI SOLUTION
VENT
OZONE GENERATOR
POWER
OXYGEN OR AIR

Figure 10. Schematic for ozonation/UV irradiation apparatus (Mauk, et al., 1976).

effects of solvents on product formation and rates of reaction (Ruzo, et al., 1974). At the present time, not much is actually known about the photochemical properties of the various PCB isomers. A few studies have shown that the primary reaction at wavelengths >290 nm is stepwise dechlorination. The actual dechlorination products have rarely been identified (Hutzinger, et al., 1971; Ruzo, et al., 1974). In 1974, a study was carried out to determine the reaction products of PCB photodecomposition in different solvents. The laboratory apparatus used to study the photodecomposition was fairly simple. Low and medium pressure mercury vapor lamps were normally used. Photolysis was carried out at temperatures from 298 to 313°K. Fifty ml of 0.005 M tetrachlorobiphenyl in either hexane or methanol solutions were exposed to UV light for 10-15 hours. HCl was observed to evolve from the solution. The products contained in the methanol solution consisted of dechlorinated PCB and certain methanol substitution products. The amount of methoxylated products did not exceed 5 percent of the total amount of products formed. It was determined that the rate of dechlorination was dependent on the extent to which the particular chlorines increased or decreased the probability of an excited state configuration of the molecule. It was concluded that the photolysis of PCBs at wavelengths greater than 290 nm indicated a possible use of this process on the industrial scale.

If photolysis is to occur, the molecule must absorb light energy above 290 nm or receive energy from another molecule through an energy transfer process. The initial step of the photolytic reaction usually involves fission of the parent molecule to form free radicals. These intermediates are unstable and react further with the solvent. Other organic molecules, inorganic species, radicals, etc., may be formed. The product may be a complex mixture in which isomerization, substitution, oxidation, or reduction processes have occurred. To date, there have not been any studies incorporating photolysis on PCB contaminated mineral oils or hydraulic fluids.

3.1.8 Reaction of PCBs With Sodium-Oxygen-Polyethylene Glycols

This process is based on the discovery that molten sodium metal in a certain solvent medium can serve as a chemical reactant. The reactivity is dictated by the mechanism of decomposition of the PCB molecule. Through extensive laboratory experimentation, it was determined that the reacting solution should be composed of 200 ml of polyethylene glycol (avg. M.W. = 400), dried over anhydrous Na_2SO_4, and 2.3 grams of metallic sodium. The temperature was raised above the melting point of the metallic sodium (370.28°K) and stirred vigorously. After the remaining droplets of molten sodium disappeared, 1 ml of PCB oil was added to the solution. The temperature of the system rose to 453°K. After 30 seconds, a gas chromatographic analysis showed approximately 95 percent decomposition of the PCB oil. The reaction evolved a large amount of H_2 gas. The small amount of sodium remaining in the solution was washed with methanol and water. Water soluble Cl^- was present. Infrared and NMR analysis showed that the PCB oil was converted to polyhydroxylated biphenyls and hydroxybenzenes. These compounds were also found to exist inthe water layer. Formation of NaCl by precipitation also occurred and was analyzed for by x-ray diffraction. Analysis of the reaction mixture by mass spectrometry showed the absence of chlorinated organic material. It was concluded by the researchers that the two ingredients essential for dechlorination of PCBs in polyethylene glycols were sodium and oxygen (Pytlewski et al., 1980). The reference gives a detailed analysis of the postulated mechanism for this reaction.

To date, this process has not been scaled up from the laboratory; however, the possibility of recovering hydrogen gas, polyhydroxylated biphenyls, and NaCl on a large scale exists.

3.1.9 The Sunohio Process

Sunohio (1980) has developed a process to break down the PCB molecule into its two primary components, biphenyl and chlorine. Organically-bound chlorine is converted to chloride. The biphenyl molecule is converted to polymeric solids. As the chemical reactions occur, the biphenyl nuclei polymerize to form chains and branched chains of biphenyl molecules. The process is called PCBX which is a Sunohio trademark. A full scale stationary model is now completed. A fully operational mobile unit is either completed or near completion at this time. This unit is designed to perform the following duties: 1) it treats the transformer oil by filtering it, removing moisture, acids, and other contaminants; 2) it removes and destroys all PCBs contained in the transformer oil but not the oil itself; and 3) it destroys pure PCBs. The equipment needed to process the PCB oil is contained in a large tractor/trailer. It is self-contained and can either generate its own power or can be hooked up to an external electrical power source.

The initial mobile processing unit is designed to handle about 1.9 m^3/hr (500 gal/hr) of transformer oils containing up to 1000 ppm of PCBs. A generalized process description is as follows. A gas chromatograph analysis is run to determine PCB content. The contaminated oil is passed through the conventional treatment facility to remove moisture and contaminants. A vacuum degasser elevates the temperature of the oil. Oil is passed through the entire apparatus and reagent is added at a rate that is consistent with the flow rate of the oil and the PCB content. The oil is heated to reaction temperature and goes to the mixing chamber where the reagent is thoroughly metered and mixed. The oil next enters the reaction vessel. After leaving the reaction vessel, it goes through a heat exchanger and exchanges heat with the oil that will enter the vacuum degasser, This cools the PCB oil to the correct temperature. It next goes through two stages of filtration. Next, it becomes the counterflow in the first heat exchanger, since it needs to acquire heat again before vacuum degassing. After the vacuum degassing step, it is returned to the transformer or held in the retention tank.

The degradation of pure PCB is similar to the above process. A quantity of oil is retained in the retention tank and continuously recycled. Pure Aroclors can be destroyed at an approximate rate of 19 liters per hour.

Overall, the process depends on the use of a commercially available reagent which abstracts chlorine atoms from the biphenyl nucleus. The specific chemical reactions are carried out under controlled conditions of process time, temperature, and reagent amount. Selective filtrations remove any excess reagent and all the products. Transformer oils can be removed from fully charged transformers and, after treatment, can be returned to the same transformer in minutes.

The goal in developing this process was to remove all the PCBs from the fluids treated. Fluids used in laboratory studies contained from 100 ppm to

10,000 ppm PCBs. The treated fluids contained 0 ppm to 40 ppm PCBs respectively after one treatment.

Optimum reaction conditions have been established for the following primary variables:

1. Reaction temperature: the temperature is well below the flash point of typical hydrocarbon fluids.
2. Reaction times: a few minutes retention time is adequate to meet process requirements.
3. Reagents: reagent amounts about four times the theoretical amount are optimum.

This process has also been applied to silicone oils. The PCBs were destroyed by the process, and the silicone fluid appeared to be unchanged. More testing is required to prove the reliability of the PCBX process for application to all silicone fluids. Specific process data are not available from Sunohio at this time.

3.1.10 Catalyzed Wet Air Oxidation

This process is based on the fact that a solution of any organic material can be oxidized by air or oxygen if enough heat and pressure are applied. Therefore, at temperatures of 423 to 613°K and 3.1 MPa to 17.2 MPa, sewage sludges will be oxidized to alcohols, aldehydes, and acids. At higher temperatures and pressures, the organic material can be oxidized to CO_2 and H_2O (Astro, 1977).

Recently, IT Enviroscience, Inc., (ITE) has developed a catalyzed wet air oxidation process for the destruction of PCBs. Their process is patented and involves the direct oxidation of PCBs by air or oxygen in an acidic aqueous medium at high temperatures. This process can be used for organic material in aqueous solution, organic liquid residues, and specific types of sludges and solid residues. Special attention was given to PCBs in the development of this process (IT Enviroscience, 1980).

This catalyzed wet air oxidation process utilizes a water soluble, single phase catalyst system. It differs from other processes in that the catalyst is homogeneous, and, unlike uncatalyzed wet air oxidation, heat and pressure are minimized in driving the dissolution of oxygen from air and the subsequent reaction with various organics in solution. The catalyst itself is used to promote the necessary oxygen transfer. The ITE catalyst systems speed up the transfer of oxygen to the dissolved state by using the gas and liquid phase reactions based on the reactions of the catalyst components with the organic material in the reactor.

The decomposition process scheme consists of a controlled stirred tank reactor containing the catalyst solution. Air and the PCB wastes are pumped into the reactor continuously. The organic materials are oxidized with the heat of reaction used to drive off water, CO_2, N_2, water vapor, any volatile organic material, and any inorganic salts formed. Condensible organic material and water are returned to the reactor. Any inorganic salts or acids formed are removed by treatment with the catalyst solution in a separate stream. Vent gases are minimal and can be treated by absorption, adsorption, or scrubbing. ITE emphasizes that the most important features of this process are than non-volatile organic materials remain in the reactor until destroyed and there is no aqueous bottoms product.

When the feed enters continuously, PCBs are added to the reactor at their steady state destruction rate. The PCBs are consumed at the same rate they are added to the system. If the catalyst solution needs disposal, the reactor will need to be batch operated to destroy the remaining organic material. Complete destruction of the organic material occurs at this point, and concentrations are reduced to ppm or ppb levels. A pilot plant is now under construction by ITE to demonstrate the process.

An alternative to the continuous process is a direct scale up of the laboratory batch reactor. In the batch process, PCBs, oxygen, and catalyst solution are fed to the reactor. The reactor is then sealed and heated. The reaction proceeds for two hours at 523°K and 6.9 MPa. Next, the reactor is cooled and vented. It is important to note that vent gas is not produced while the PCBs are being destroyed. The cycle is then repeated again. After six batches, the HCl produced by the oxidation is distilled from the reactor. In order to destroy residual PCBs in the catalyst solution, the reactor should be run for 12-24 hours, approximately once a week.

Both of these catalytic wet oxidation processes, continuous and batch, have been shown in laboratory scale tests to be able to destroy at least

99 percent of the PCBs. There are several programs under way to commercialize and scale up these processes. Figure 11 depicts the process schematic for PCB destruction by catalyzed wet air oxidation.

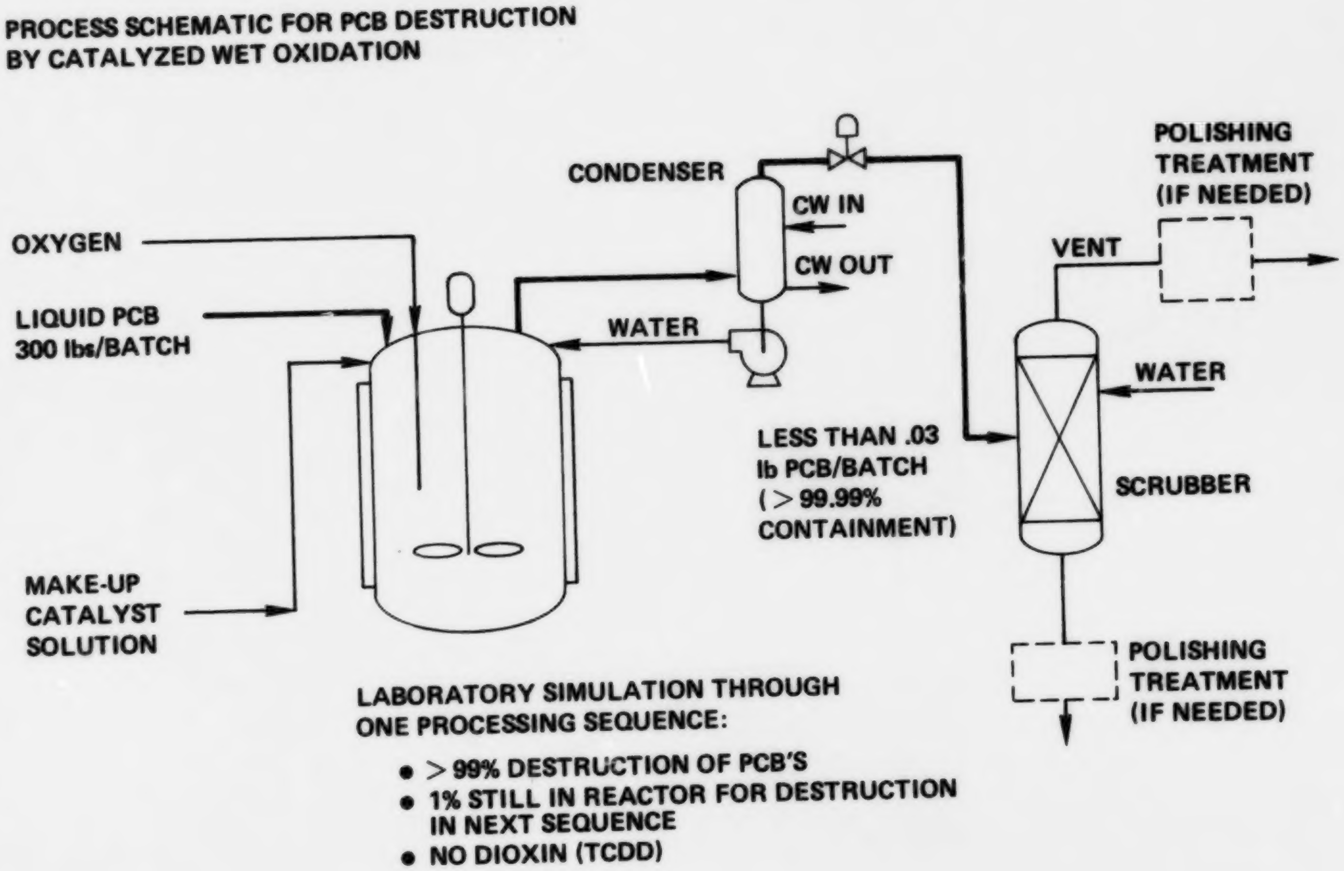
3.2 BIOLOGICAL METHODS

The hydrophobic characteristics of PCBs promote their adsorption from aqueous solution onto available surfaces. The type of surface determines the amount of PCBs being adsorbed (Hague, et al., 1974). Hague and Schmedding (1976) studied the adsorption characteristics of three PCB isomers by a few different adsorbents and concluded that adsorption increases as the number of chlorine atoms on the molecule increases. Current information indicates that PCBs have a strong adsorption attraction towards soil and that the organic matter content of the soil and the chlorine content of the PCB molecule are the primary factors affecting adsorption. Laboratory tests have shown that PCB degradation by microorganisms in the soil could be an effective process for PCB elimination (Briggs, 1973; and Scharpenseel, 1978).

The above studies indicate that PCBs are biodegradable to a certain degree and can be attacked by soil microorganisms. Studies indicate that an enriched culture of soil microorganisms could degrade PCBs at an appreciable rate. Biological methods would generally apply to dilute aqueous systems only. A precise value for the solubility of PCBs in water is extremely difficult, if not impossible, to determine since PCBs found in transformer and capacitor dielectric mineral oils. For example, the solubilities of Aroclors 1016, 1221, 1242, 1254, and capacitor fluid at room temperature were found to be 906 ppb, 3516 ppb, 703 ppb, 70 ppb, and 698 ppb, respectively (Griffin, et al., 1980). Additional studies need to be carried out to determine the effects of microoorganisms on the PCB degradation process. In most studies, only the more water-soluble PCB isomers were used. Since water soluble and total PCBs have different proportions of PCB isomers (Hague, et al., 1974), no conclusive evidence regarding microbial degradation of PCB contaminated capacitor or transformer fluids can be presented.

3.2.1 Activated Sludge Methods

Activated sludge processes are used for treatment of wastewater. Complete aerobic treatment without sedimentation is carried out as the wastewater



PROCESS SCHEMATIC FOR PCB DESTRUCTION BY CATALYZED WET OXIDATION
OXYGEN
LIQUID PCB 300 lbs/BATCH
MAKE-UP CATALYST SOLUTION
CONDENSER
CW IN
CW OUT
WATER
LESS THAN .03 lb PCB/BATCH (> 99.99% CONTAINMENT)
VENT
POLISHING TREATMENT (IF NEEDED)
WATER
SCRUBBER
POLISHING TREATMENT (IF NEEDED)

LABORATORY SIMULATION THROUGH ONE PROCESSING SEQUENCE:

- > 99% DESTRUCTION OF PCB'S
- 1% STILL IN REACTOR FOR DESTRUCTION IN NEXT SEQUENCE
- NO DIOXIN (TCDD)

Figure 11. Process schematic for PCB destruction by catalyzed wet air oxidation (IT Enviroscience, 1980).

is continuously fed into an aerated tank where microorganisms digest and flocculate the organic waste. The microorganisms (activated sludge) settle from the aerated liquor in a final clarifier and are returned to the aeration tank. The effluent emerges from the final settling tank purified. Activated sludge treatment is classified as an aerobic treatment process because the microbial solution is suspended in a liquid medium containing dissolved oxygen. It is important that aerobic conditions be maintained in the aeration tank. Dissolved oxygen extracted from the liquor is replenished by air to the aeration tank. The various engineering unit processes are: sedimentation basin, aeration basin, clarifier, sludge dewatering, and chemical storage.

Tucker, Litschgi, and Mees (1975) did some work with a continuous feed activated sludge unit. With a feed rate of 1 mg/48 hrs, they reported an 81 percent degradation of Aroclor 1221, 33 percent degradation of Aroclor 1016, 26 percent degradation of Aroclor 1242, and 15 percent degradation of Aroclor 1254. With Aroclor 1221, only the 3-, 4-, and 5-chlorine isomers were not degraded. Mihashi, et al. (1975) reported 50 percent PCB degradation in activated sludges. He also reported that the degree of PCB degradation decreased as chlorine substitution onto the rings increased. It was also found that the degradation of water-soluble Aroclor 1242 by mixed cultures of soil microorganisms occurred in a short period of time. The lower chlorinated isomers were more readily degraded than the higher chlorinated isomers. The rates of degradation ranged from the monochloro isomers which were degraded 100 percent within 6 hours to the tetrachloro isomers which were degraded 42 percent after fifteen days. The major microorganisms found in the activated sludge were alkaligenes odorans, alkigenes denitrificans, and an unidentified type of bacterium. Figure 12 is a flow diagram of the activated sludge process.

3.2.2 Trickling Filter Methods

Trickling filters are another biological treatment option for the degradation of dilute aqueous organic waste streams only. The filter consists of crushed rock, slag, or stone. These materials provide a surface

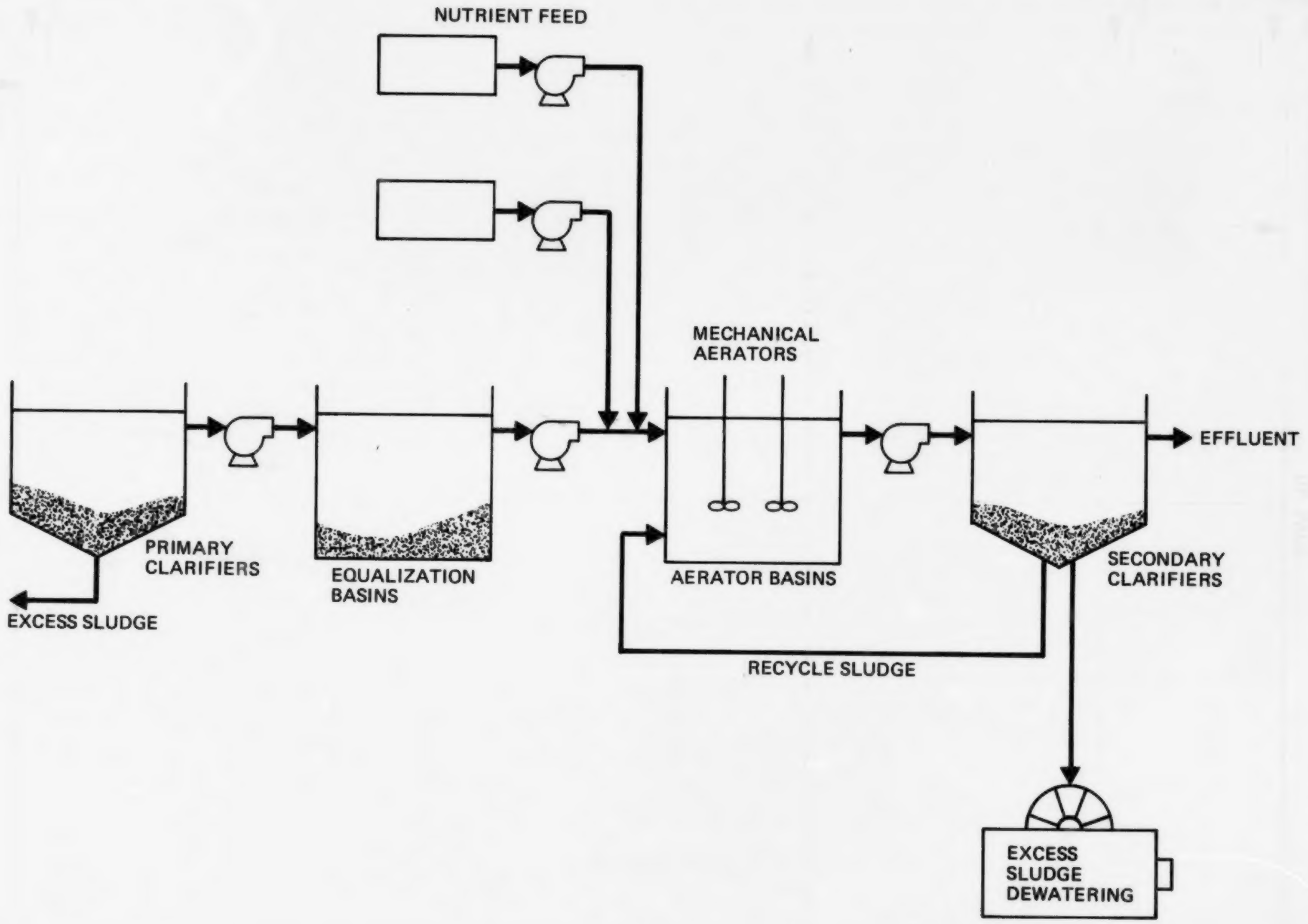

NUTRIENT FEED
MECHANICAL AERATORS
EFFLUENT
PRIMARY CLARIFIERS
EQUALIZATION BASINS
AERATOR BASINS
SECONDARY CLARIFIERS
EXCESS SLUDGE
RECYCLE SLUDGE
EXCESS SLUDGE DEWATERING

Figure 12. Flow diagram of activated sludge process (Hansen, et al., 1978).

for biological growth and passages for liquid and air. The primary treated waste flows over the microbial surface. The soluble organic material is metabolized and the unsoluble material is adsorbed onto the media surface (Wilkinson, et al., 1978). The biological components are bacteria, fungi, and protozoa. The bottom portions of the filter contain nitrogen fixing bacteria. The major components of a trickling filter are a rotary distributor, an underdraw system, and filter media. Influent waste water is pumped into the rotary distributor for uniform spreading over the filter surface. The rotary arms are driven by the reaction of the waste water flowing out of the distributor nozzles. The effluent is carried away by the underdraw, and air is circulated through the bed. The quantity of biological slime produced is controlled by the amount of organic waste available to digest. The maximum growth is controlled by various physical factors including hydraulic dosage rate, type of media, type of organic matter, amounts of nutrients present, and the nature of the particular biological growth.

Trickling filters are classified as either low (standard), intermediate, high, or super rate filters, based on hydraulic and organic loading rates. Since an aqueous medium is necessary, only dilute soluble PCB isomers may readily be contacted with the active microbes. In the general case, PCBs comprising mineral oil dielectric fluid and capacitor fluids will not be degraded by the active microbes, since their solubility in water is extremely low. Figure 13 is a flow diagram of high rate trickling filter process.

3.2.3 Special Bacterial Methods

A few newer biological disposal systems are currently being developed to improve the performance of trickle filters and activated sludge reactors. These newer processes are mainly untried as disposal techniques.

Biodisc treatment is a type of thin film biodegradation in which large plastic discs are partially submerged in the aqueous waste solution. The aerobic microorganisms colonize the disc surfaces and are oxygenated as the discs are rotated. A well aerated surface is created by arranging a line of discs in series. This creates a well aerated surface requiring little space for biological activity (Autotrol, 1971).

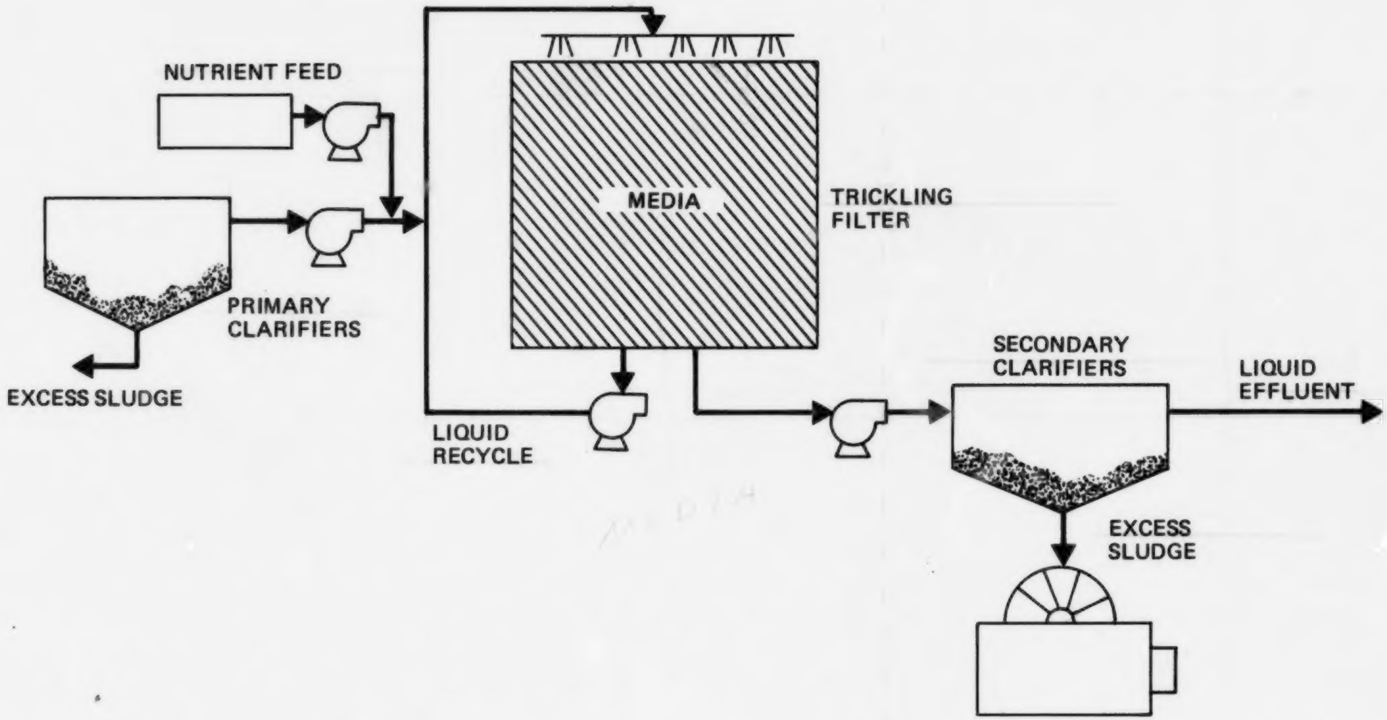

NUTRIENT FEED
MEDIA
TRICKLING FILTER
PRIMARY CLARIFIERS
EXCESS SLUDGE
LIQUID RECYCLE
SECONDARY CLARIFIERS
LIQUID EFFLUENT
EXCESS SLUDGE

Figure 13. High rate trickling filter flow diagram (Hanson, et al., 1978).

The Bio-surf^{TM} process has been added to facilities to upgrade the effluent treatment system. Anerobic conditions can be created by enclosing a submerged Bio-surf system and adding a carbon source such as methanol (Autotrol, 1974).

Ecolotrol, Inc., has developed a full scale biological fluidized bed process, utilizing sand as the particle growth medium. A large population of microorganisms makes possible a faster treatment than conventional biological treatments such as activated sludge or trickle filters. A clarifier is not required with the Ecolotrol system. These units have been used on municipal wastes and on a pilot plant scale for processing pharmaceutical and petroleum tank truck wastes (Wilkinson, et al., 1978).

Wornes Biochemicals has developed a freeze dried biochemical solution containing mutant bacteria and various substances to facilitate their growth. Various chlorinated benzene derivatives including hexachlorobenzene have been degraded (Phenobac^{TM}, 1977).

None of these processes have been directly applied to non-aqueous systems. Because of the insolubility and stability of the PCB molecule, adaptability of these processes to the immediate problem of PCB degradation in non-aqueous materials will be difficult.

4. EVALUATION OF PHYSICOCHEMICAL PROCESSES

4.1 ADSORPTION PROCESSES

As stated in Chapter 3, activated carbon adsorption processes are applied primarily to aqueous streams. An extensive literature search was carried out to find information on activated carbon adsorption processes applied to PCB removal from heat transfer fluids. This search did not uncover any pertinent information. The U.S. Air Force (U.S. Air Force 1976) funded studies on using activated carbon to remove TCDD from Herbicide Orange provided most of the background information for non-aqueous carbon adsorption processing methods. The following treatment is based on procedures used in the Herbicide Orange study. Direct applications of this process to the disposal of PCBs may be possible. It is worthwhile to evaluate and assess the merits and downfalls of the U.S. Air Force study.

4.1.1 Technical Factors

From a technical point of view, adsorption processes for removing hazardous compounds from liquid streams are attractive because of the possibility of resource recovery. In other words, it may be possible to remove the PCBs from a mineral oil dielectric fluid and reuse the purified mineral oil.

4.1.1.1 State of Technology--

Activated carbon adsorption technology is well developed for aqueous stream purification and is used widely for municipal water purification. Adsoprtion techniques are not well defined for non-aqueous systems at this time. As stated in Chapter 3, activated carbon was used to remove TCDD with an average concentration of 2 ppm from Herbicide Orange. TCDD was reduced to 0.1 ppm or less, and the process was considered successful. The U.S. Air Force concluded that the technology to dispose to the TCDD contaminated activated charcoal did not exist, so the Herbicide Orange stocks were incinerated at sea (Ackerman, et al., 1978).

4.1.1.2 System Design--

The reprocessing plant would consist of the following units:

- Mineral oil storage tanks
- Heating tank
- Boiler to provide steam to the heating tank
- Activated charcoal cartridges
- Product tanks
- Appropriate pump, filters, piping, etc.

Overall processing should be evaluated as to the performance or operating characteristics of each individual unit.

4.1.1.2.1 Pretreatment and feed--The feed will be a mineral oil contaminated with PCBs, possible acids, and other trace substances, such as metals and inerts. These should be removed before contact with major processing equipment. Conventional pretreatment technologies could be used for this purpose. An activated carbon adsorption facility typically has minimal pretreatment equipment since most noxious materials will be adsorbed onto the activated carbon.

4.1.1.2.2 Processing--Unit processes of principal interest to PCB disposal and those requiring evaluation are the heating tank, the adsorption columns, the filtering process, and the process tanks.

The PCB material in the heating tank will have to be evaluated carefully. The PCB oil will be heated and sent to the carbon adsorption columns, so the optimum processing temperature should be determined carefully.

Column performance should be evaluated for optimum charcoal pellet size, texture, and composition. Pressure drops and flow rates must be assessed to insure smooth operating. Test runs with alternate types of activated charcoal should be carried out to determine optimum column efficiencies. Adsorption cartridge configuration is an important operating variable and must be evaluated critically. The adsorption cartridges should be operated in a series configuration for best results. Pilot plant studies will be needed to study the proper amount of carbon needed for PCB removal. A process control scheme must be developed for the cartridge configuration to control the flow direction so any cartridge can be made first, second, etc., in the series. Expended cartridges must be removed, so the cartridge replacement method must be developed to efficiently replace the old cartridge with a minimum risk of accidents. This will insure that the PCB material is further treated by new carbon, thus increasing the PCB reduction. When the used cartridge is removed from the system, it should be sealed at both ends to insure against PCB or other hazardous material leaks.

Pilot plant studies are needed to define the necessary process parameters such as flow rates, temperature, pressures, as well as types of pumps, filters, heat exchangers, etc. The process parameters will depend on the type of PCB waste to be detoxified.

4.1.1.2.3 Pollution control--The use of activated carbon filters on all vents, leak-free pumps, and plumbing, coupled with the use of sealed cartridges, should prevent any escape of PCB material to the environment. Every effort should be made to minimize the release of vapors from the various units and from the dedrumming facility. All equipment that contacts the PCB material should be sized properly to avoid potential leaks or spills. The plant engineering should be such that potential problems will be minimized, and contingency plans should be developed to reduce the consequences of accidents from faulty pollution control equipment. All cartridges should be made of new steel to prevent ruptures. The weight of the column should determine what type of equipment should be utilized in removal/replacement of the cartridges. Charging the cartridge with carbon and the PCB oil must be done very carefully. It will be necessary that the cartridge is charged before being put on stream. The plant, from the process tanks to the filling of drums with products, should be designed for closed loop containment of vapors. If vapor exhaust is required, it should be run through carbon filters.

There will be no liquid effluent produced in this process. No water or solvent is used in the reprocessing plant. The used adsorption cartridges and air-scrubbing carbon filters must be sealed and prepared for placement in a recoverable storage structure. Upon completion of the process, the plant facilities should be cleaned with solvent.

4.1.1.2.4 Destruction efficiency--Since activated carbon adsorption processes have not been applied to removal of PCBs from heat transfer fluids, destruction efficiencies cannot be estimated. PCBs would not actually be destroyed but will be adsorbed onto the charcoal for further processing. Destruction efficiencies do not really exist as such for this process. Based on the U.S. Air Force funded study on TCDD removal from Herbicide Orange, it may be expected that PCB removal could be as high as 95%. It is doubtful whether any activated carbon absorption process will be capable of destruction efficiencies equivalent to those of Annex I incinerators or high efficiency boilers.

4.1.1.3 Process Controls--

There are five major operations in an activated carbon adsorption process that will need to be controlled:

- Dedrumming the PCB material and pumping it into plant storage tanks
- Heating and processing the PCB material including cartridge changing
- Redrumming the finished product
- Removal of the contaminated carbon cartridges and air filters from the reprocessing system, and preparation of them for recoverable storage
- Disposal of empty mineral oil drums and other contaminated material

Each one of these major operations must be evaluated in terms of what type of process control schemes are used to regulate the particular operation. Process control should focus on creating a failsafe disposal method for the PCBs.

Temperature control is necessary in all heating tanks. Optimum adsorption will occur at a specific temperature. Heat exchangers or heating elements must be controlled to maintain proper operating conditions.

Flow rates will also need to be controlled to insure smooth and steady operations. Adequate flow controllers should be installed downstream of all critical pumps.

Each activated carbon adsorption facility will need to be evaluated separately for overall control of important process variables. The process control scheme should adequately eliminate guesswork and risk in operating the overall disposal process.

4.1.1.4 Effluent Monitoring--

Air quality monitoring could be done in several different ways: 1) use of ambient air samplers placed at specific locations around the reprocessing plants, 2) use of biomonitoring plants located at various areas around the facilities, and 3) visual observations of native flora in the general vicinities of the reprocessing plants. All the air sampling instruments used should have a high demonstrated efficiency under field conditions. Periodic air samples should be collected and analyzed for PCB content and total composition. In addition, post-operational samples should be collected and analyzed.

As mentioned earlier, there will be no aqueous waste streams nor release of any raw or processed PCB material to surface or groundwaters. Processed PCB oil will be transferred directly to drums and transported by rail or truck.

4.1.1.5 Waste Characterization --

Activated carbon adsorption processes are best suited to handle aqueous streams, contaminated with PCBs. Municipal water treatment plants currently utilize this technology for waste treatment. If the process is to be adapted to non-aqueous waste treatment, certain modifications of the basic design will need to be incorporated into the overall process scheme.

4.1.1.5.1 Range of PCB concentrations--No information on tolerable levels of PCBs was found. Aqueous purification systems will contain very dilute amounts of PCBs, perhaps at ppb levels. Based on the U.S. Air Force funded study on Herbicide Orange, a similar activated carbon adsorption purification system should be able to be developed to handle PCB transformer fluids with a PCB concentration of greater than 500 ppm.

4.1.1.5.2 Limitations on constituents--PCB wastes containing excessive concentrations of toxic heavy metals will require pretreatment prior to entering the adsorption column. The extent and type of treatment will depend on the nature of the metals. Any contaminants that could cause fouling or corrosion of process equipment may also need to be eliminated or reduced by pretreatment. Any substituent that could interfere with the charcoal adsorption process will also need to be eliminated by pretreatment.

4.1.2 Environmental Factors

Because no references on disposal of non-aqueous PCBs by activated carbon adsorption treatment were found, it is difficult to estimate the environmental impacts of this process.

4.1.2.1 Potential Impacts of Disposal Operation--

During reclamation, the use of activated carbon filters on all the vents, plumbing, and sealed cartridges should prevent any significant escape of the PCB material to the air. Operations that could result in the release of toxic material to the air are:

- Dedrumming the PCB material and pumping it into storage tanks
- Heating and processing the PCB material including cartridge charging
- Redrumming the finished product
- Removal of the contaminated carbon cartridges and air filters from the reprocessing system, and preparation of them for recoverable stroage
- Disposal of empty drums and other contaminated equipment

Operations 1 and 3 would involve transfer of the PCB material at or near ambient temperatures. Because of the low volatility of PCBs in this temperature range, the potential impact should be minimal. Operation 2 requires heating the herbicide and maintaining it at this temperature during the low-pressure adsorption process. The environmental impact from this step could be signficant since the volatility of the PCB material will be increased by heating. Process accidents at this stage could result in the release of high quantities of PCB to the atmosphere.

Operation 4, removal and preparation of the contaminated carbon cartridges and air filters for storage has minimal potential for introducing PCBs into the atmosphere. The cartridges will be closed to the environment before removal from the system. Operation 5 involves dismantling and disposal of the parts of the dedrumming and reprocessing equipment that come in contact with the PCB material. This material will have only low levels of contamination since it will be reused or flushed with a suitable solvent following completion of reprocessing. Overall, there will probably be small quantities of PCBs released into the atmosphere during reprocessing. An evaluation of the process should include extensive air sampling using sensitive analytical methods.

Since during reprocessing there will be no aqueous waste streams, nor release of any raw or processed PCB oil to surface or groundwaters, there should not be any impact on water quality. The only possible impact on water quality would be in the event of a spill directly into drainage ditches from storage to the reprocessing plant. This risk could be minimized if strict precautions are taken to prevent accidental spills. Storage of carbon cartridges and filters pose no anticipated impacts on water quality.

4.1.2.2 Potential Impacts of Disposal of Process Wastes--

Overall, environmental impacts of the disposal of process wastes should be very low with the use of additional engineering constraints such as carbon-filtered vents and leak free pumps. These should be incorporated to eliminate discharge of the PCBs to the ambient air. There should be minimum impact from discharges to the air from drum disposal if the drums are crushed after drainage of the solvent. The crushing will reduce the possibility of residual PCBs entering the environment while the crushed drums await shipment to a steel manufacturing plant. The environmental impact associated with the storage and transport of these drums should not be significant. Evaluation should focus on each unit process separately and on the associated risks of each one. Extensive monitoring and sampling will have to be done to determine possible toxic material escape points. As stated earlier, there should not be any anticipated impacts on water quality from the reprocessing units.

4.1.2.3 Potential Impacts of Accidents--

Accidental spills or leaks of PCBs from an activated carbon adsorption facility may pose the following threats:

- Contamination of surface or groundwater

- Contamination of land areas where humans, animals, or croplands could be exposed
- Contamination of areas that could lead to significant airborne movement of PCBs
- Contamination of surface or groundwater if the PCB oil is discharged directly into the environment.

Facilities disposing of PCBs must have spill prevention contingency plans. These plans should include spill control strategies and countermeasures. These plans should detail safe handling procedures of the PCB material. The goals of these plans are to prevent discharges and to minimize impacts of spills. An adequate SPCC plan should minimize the potential for spills and hence, potential environmental impacts from spills. The typical activated carbon adsorption treatment plant is not in the hazardous waste disposal business. It is not expected that such a plant will be constructed in accordance with RCRA standards for hazardous waste disposal facilities. Because of the threat to the environment of potential PCB spills, an activated charcoal adsorption treatment facility should be evaluated carefully with respect to PCB storage and containment. It is recommended that adequate storage, as mandated by PCB regulations 40 CFR 761.42, be provided before the facility is approved.

4.1.3 Economic Factors

Capital and first year operation costs for a typical activated carbon adsorption facility are depicted in Tables 4 and 5. Since this process has not been directly applied to PCB disposal in non-aqueous streams, a cost analysis cannot be done at this time. It may be possible to use the following data as a guide for determining whether or not an activated carbon adsorption process is worthwhile.

The most costly unit process is the carbon adsorption columns together with the regeneration system. The total capital cost for a $0.31 \frac{m^3}{sec}$ facility was $1,205,423 based on mid-1978 dollars. Energy and chemical requirements comprise over 90% of the direct operating costs. The total first year operating costs including administrative overhead was $4,623,416 (based on mid-1978 dollars).

Possible credits could exist for the processed PCB material, though this will depend on the overall effectiveness of the adsorption process.

TABLE 4. SUMMARY OF CAPITAL COSTS FOR CARBON ADSORPTION
(Hansen et al, 1978)

Capital Cost Category Module	Costs						Quantities	
	Site Preparation	Structures	Mechanical Equipment	Electrical Equipment	Land	Total	Land (ft^2)	Other Steam lbs/hr
Carbon adsorption	$ 11,400	$ 52,900##	$ 552,000	$ 552	$ 3,430	---	4,620	---
Steam generator	13	1,163	12,900	--	124	---	167	664
Waste pump	---	---	10,800	--	---	---	---	---
Piping	1,125	---	72,500	--	---	---	---	---
Total	12,538	54,063	648,200	552	3,554	---	4,787	664
Supplemental capital Costs	---	141,303	---	--	---	---	---	---
Subtotal of capital costs	---	---	---	--	---	$ 860,210	---	---
Working capital**	---	---	---	--	---	302,202	---	---
AFDC‡	---	---	---	--	---	43,011	---	---
Grand total of capital costs	---	---	---	--	---	1,205,423	---	---

* Scale = 5,000 gpm

† Mid-1978 dollars

# Building

** At one month of direct operating costs

‡ Allowance for funds during construction at 5% of capital costs

## Includes initial carbon charge

TABLE 5. SUMMARY OF FIRST YEAR OPERATING AND MAINTENANCE COSTS FOR CARBON ADSORPTION
(Hansen et al, 1978)

	Costs†							
	Labor							
O&M Cost Category Module*	Type 1 Operator 1 ($7.77/hr)	Type 2 Operator 2 ($9.19/hr)	Type 3 Laborer ($6.76/hr)	Energy Electrical ($0.035/KWH)	Maintenance Costs	Chemical Costs	Total	Other KWH (yr)
Carbon adsorption	35,260	10,396	40,857	2,100,000	119,000	1,290,000	---	3,744,000
Steam generator	590	105	7,793	5,280	---	6,170	---	---
Waste pump	---	---	---	8,630	---	---	---	---
Piping	---	---	204	---	363	---	---	---
Total	35,850	10,501	48,854	2,113,910	119,363	1,296,170	---	3,744,000
Supplemental O&M costs	---	---	---	---	1,770	---	---	---
Subtotal of direct O&M costs	---	---	---	---	---	---	3,626,418	---
Administrative overhead#	---	---	---	---	---	---	725,284	---
Debt service and amortization**	---	---	---	---	---	---	247,606	---
Real estate taxes and insurance‡	---	---	---	---	---	---	24,108	---
Total first year operating costs	---	---	---	---	---	---	4,623,416	---

* Scale = 5,000 gpm
† Mid-1978 dollars
# At 20% of direct operating costs
** At 10% interest over 7 years
‡ At 2% of total capital

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Generally, it appears that activated charcoal adsorption processes for removal of PCBs from heat transfer fluids will require moderate capital investment and operating costs with a possible resource recovery credit.

4.1.4 Energy Factors

Activated carbon regeneration will take up the greatest proportion of energy requirements. It is estimated that 0.46J/m^3 of energy needed for 0.31 m^3/sec (5,000 gpm) process. Energy factors for the process adapted to the non-aqueous disposal of PCBs cannot be developed at this time, but will need to be developed if the process is to be applied.

4.2 CATALYTIC DEHYDROCHLORINATION

4.2.1 Technical Factors

4.2.1.1 State of Technology--

Catalytic dehydrochlorination of PCBs is a proven research method that has not been scaled up. The results of a major study on Aroclor 1248 indicate that chlorine can be catalytically removed from the PCB molecule and replaced by hydrogen to produce non-toxic hydrocarbons (Lapierre et al. 1977). This study has created a foundation for commercialization of this process.

4.2.1.2 System Design--

4.2.1.2.1 Pretreatment and feed--Feed stream characterization of PCB mixtures is extremely difficult because of the possibility of 210 isomers existing in solution. Aroclor 1248 was used in the studies of Lapierre et al., (1977). Materials to be treated should first be charged to a rotary extractor. The PCB material to be dehydrochlorinated is extracted with hot ethanol and pumped to the main reactor. This extraction is necessary to separate the organic materials to be reacted from possible contaminants and inert substances. Before the PCB material enters the reactor, the reactor contents should be boiled at atmospheric pressure to evaporate the ethanol. The ethanol should then be condensed and returned to the extractor until the inert materials still in the extractor are free of PCB residues.

4.2.1.2.2 Processing--Process design must consider choices between alternative process steps, equipment types, and various parameters such as sizes, temperatures, pressures, residence times, flow rates, etc. A decision would have to be made between implementation of a batch process or a continuous process. A continuous process works best when a steady flow of feed of uniform composition is available. This may not be the case in PCB processing. A batch process may have to be utilized in at least the initial stages of process development. The need for extremely high temperatures and possible problems with thermal degradation of the products indicate the processing should be done in the liquid phase in a suitable solvent.

Solvent selection is crucial to this process. The solvent must be adaptable to both the PCB molecule and to the acid acceptor which is needed to reduce corrosion and to produce a clean effluent. The solvent must be capable of being separated and recovered by distillation and should be fairly inexpensive.

Operating temperature is a critical design parameter. Reaction at high temperatures results in greater solubility of the PCBs, reduction in the size of equipment, and a faster reaction. However, as more heat is required, the total pressure required to raise the hydrogen partial pressure will need to be increased.

The extraction step should be carried out at atmospheric pressure to reduce equipment design complications. Dehydrochlorination should be accomplished at high hydrogen pressures to insure adequate reaction rates. Hydrogen partial pressures should be between 2-5 MPa.

Catalyst selection should be determined by the process requirements. Catalyst life will vary according to the types of impurities found in the feed and the severity of the reaction conditions. How well the catalyst can be regenerated and its life span are important economic considerations. Particle size and overall catalyst configurations need to be considered when doing an activity study.

An acid acceptor is needed to reduce the corrosiveness of HCl. Also, HCl should be neutralized by the acid acceptor in order to reduce waste emissions.

4.2.1.2.3 Pollution control--Possible pollutants are HCl, hydrocarbons, other simple chlorinated compounds, and salt. Appropriate pollution control devices would have to be installed to eliminate or reduce these wastes. Absorption or scrubber units could be used to effectively control the elimination of HCl. The hydrocarbons and other organic species should be separated from the waste stream by liquid-liquid extraction. As an alternative to pollution control, the waste materials could be utilized for energy, chemicals, or solvents elsewhere.

4.2.1.2.4 Destruction efficiency--The study carried out by Lapierre, et al.(1977), indicates complete conversion of PCBs into dechlorinated biphenyls. High destruction efficiency may be assumed to be possible upon scale up of this process.

4.2.1.3 Process Controls--

Important variables which need to be controlled are: temperatures, pressures, flow rates, liquid level and composition. The measurement equipment must give an accurate display of the desired variable. The type and location of measurement and control equipment will need to be specified upon scaleup. The temperature of all incoming streams must be monitored and controlled, as temperature is perhaps the most important process variable affecting the level of PCB conversion. Temperature and, therefore, heat supplied to the reactor must remain within the optimum operating range. An accurate control device should be installed for this purpose. Pressure drops across the pollution control system and across the individual process units should be measured and controlled. Abnormal pressure drops may drastically affect the overall process. Flow rates of all important process streams should be measured and recorded. Flow rates can be measured by use of an orifice plate, sonic type of flowmeter, or rotometer. Flow rates should be measured downstream of any pumps and in-line filters and upstream of any flow control valves. Liquid levels in all storage tanks should be monitored periodically to prevent overflow and to insure adequate flow of these fluids to the process. Either gauge glasses or automatic sensors could be used. Composition of the reactor solution should be controlled by adjusting appropriate flow rates to the reactor. A more elaborate examination of required process controls cannot be done until scaleup studies are underway.

4.2.1.4 Effluent Monitoring--

Careful effluent monitoring is needed to determine the extent of PCB conversion and to determine the potential environmental impacts of any undestroyed PCBs.

Liquid effluent streams must be monitored for PCB content and for the existence of HCl and other simple chlorinated compounds. Conventional monitoring devices such as chromatographs and spectrometers should be used to examine periodic samples from all effluent streams. If a scrubber is used, its effluent should be monitored and sampled on site and analyzed in the laboratory. Liquid effluents should also be monitored for salt content and dissolved solids.

No limit on the PCB content of scrubber water streams is given except indirectly through reference to applicable effluent or pretreatment standards and any other State or Federal laws and regulations. There is no limit, explicit or implicit given for the maximum PCB content of a solid residue stream. The effluent monitoring capability of a facility is determined by the facility operator's description of the appropriate streams.

Prior to sampling any liquid stream, plant data concerning that stream must be available. Tap sampling should be used to monitor flowing liquids or liquids in tanks or drums. Automated samplers are available which can sample almost any process stream. Use of these samplers increases the likelihood that a representative sample will be obtained.

Any vent gases should be monitored by using ambient air samplers. Periodic air samples should be collected and analyzed for PCB content and overall composition.

Any solid wastes should be sampled by a grab technique. The adequacy of the solid sampling locations should include consideration of homogeneity and amount of solid waste acquired.

4.2.1.5 Waste Characterization--

4.2.1.5.1 Range of PCB concentrations--The catalytic dehydrochlorination process should be able to handle a wide range of PCB contaminated material provided that they are in the liquid state. Transformers with a PCB concentration >500 ppm as well as PCB capacitors and mineral oil dielectric fluids with PCB content 50-500 ppm should be treatable by this process.

4.2.1.5.2 Limitations on constituents--The feed must be in either liquid or gaseous form. Inorganic and inert constituents should be removed prior to processing. Any substances that could interfere with the dehydrochlorination reaction or which could cause corrosion or fouling of process equipment should be eliminated. PCB solubility in ethanol is an important process variable, so any component in the feed stream that could alter this solubility must be contained. Commercialization of this process will elucidate other possible limitations on constituents.

4.2.2 Environmental Factors

4.2.2.1 Potential Impacts of Disposal Operation--

The potential impacts of the disposal operation appear to be minimal. Product recovery of process wastes is a viable way of lessening potential environmental impact. If the product turns out to be a fairly pure organic liquid, refining may be used to produce convenient raw materials. In this case, potential environmental impacts will be greatly reduced. If the product is a complex mixture of hydrodechlorinated hydrocarbons, it may be necessary to mix the solution with fuel oil and burn it in a furnace. If chloride residues are significant, incineration may also be necessary. This situation will greatly increase the potential for environmental damage. If any solids exist in the waste streams, landfill dumping might be necessary, and standard soil and toxicity studies would need to be carried out.

4.2.2.2 Potential Impacts of Disposal of Process Wastes--

According to current studies, a properly designed process should not produce toxic off-gases or contaminated aqueous residues. A meaningful assessment of toxicity has not been made yet. The effect of the partially and totally dechlorinated products on the environment will have to be evaluated in the overall assessment of the process. The commercial utility of the waste products will also need to be determined in an environmental assessment so decisions can be made between disposal or reprocessing.

4.2.2.3 Potential Impacts of Accidents--

Accidental spills and leaks from PCB containing products such as transformers during transportation and storage appear to be the greatest sources of accidents. The possibility of environmental contamination of the atmosphere from PCB losses from all processing units must be examined closely in scaleup studies. All pressurized units must have appropriate safety systems. Hydrogen gas is extremely flammable and volatile, and caution must be exercised when working around this equipment. Common sense safety practices should be able to prevent most accidents.

4.2.3 Economic Factors

There are no economic data available to permit an economic assessment of the proposed dehydrochlorination conversion process. It is obvious though that the hydrocarbons produced by this process would be much more expensive as fuel oil than other commercial sources. An economic evaluation must await development of engineering cost estimates. Qualitatively it appears that capital investment and operating costs would be moderate, and hydrocarbons could be recovered and sold to make the process more cost effective.

4.2.4 Energy Factors

Since this process is primarily operated for PCB disposal, the amount of energy required per unit weight of PCB destroyed must be calculated. Lack of data prohibits this calculation at the present time. It must also be determined whether or not energy credits may be gotten by recovering some or all of the heat content of the PCB waste to use for steam production.

4.3 CHLORINOLYSIS

4.3.1 Technical Factors

4.3.1.1 State of Technology--

Chlorinolysis has not been directly applied to PCB, however, the process may be adaptable. The AG Hoechst chlorinolysis process described in Chapter 3 can handle certain chlorinated benzene derivatives on a limited scale . Chlorinolysis has been successfully commercialized.

4.3.1.2 System Design--

Important system design factors are: pretreatment of the feed, the reaction and reactors, distillation, HCl absorption, and incineration of waste residues.

4.3.1.2.1 Pretreatment and feed--The waste cannot be introduced directly into the process equipment, but must be pretreated first. Light ends may contain water which must be removed by a drying unit. Solids contaminated with soot or other contaminants must be removed in a falling film evaporator unit. The waste feed system includes all equipment used to process the PCB wastes from the point of storage to the point of entrance to the reactor. The drying unit should consist of at least two adsorbers and one regeneration system. The feed can consist of a wide variety of chlorinated species, however, the aromatic content should not exceed 5% calculated as benzene.

4.3.1.2.2 Processing--The process is almost completely enclosed. Generally, a low quantity of chlorine is consumed,and low quantities of HCl are produced. An example of the effectiveness of this process is illustrated by the following stoichiometric equation:

$$1 \text{ kg residue} + 2.73 \text{ kg } Cl_2 = 3.010 \text{ kg } CCl_4 + 0.72 \text{ kg HCl}$$

This reaction is more than 95% complete using a pressure of 20 MPa and a temperature of about $873^{o}K$. Any heavy ends which are not completely converted must be separated from the reaction products in the first distillation column and recycled back to the reactor for final conversion. The second distillation unit separates the reaction products, HCl, CCl_4, and various other residues that have not been completely converted. The adsorption column produces a 31% HCl solution and must be operated adiabatically. It is important to note that all the chlorolysis reactions are exothermic. The final temperature is controlled by an excess of chlorine and should not exceed $893^{o}K$.

4.3.1.2.3 Pollution control--Waste gases containing Cl_2 and HCl must be removed in an absorption unit. This same absorption unit also functions as an emergency and normal shutdown system for the plant. Since incineration is used to eliminate the chlorine residues, attention must be paid to pertinent government regulations. During incineration, HCl, CO_2, CO, and H_2O are formed. If the incineration unit functions improperly, trace amounts of chlorine gas may also be formed. Important design parameters such as residence time, temperature, and stack height must be calculated accurately.

4.3.1.2.4 Destruction efficiency--The destruction efficiency defined as:

$$DE = 100 \frac{PCB_{in} - PCB_{out}}{PCB_{in}}$$ can only be assumed to be very low for chlorinolysis, since the destruction efficiencies of other polychlorinated aromatic compounds are very low.

4.3.1.3 Process Controls--

Four important process control variables must be manipulated to achieve adequate control of this system. They are: temperature, pressure, flow rate, and liquid level. These variables must be measured, and suitable equipment must be used to regulate them.

The incinerator must be equipped with process controls to regulate waste and air flows to insure proper combustion conditions such as temperature and oxygen level. The incinerator must also be equipped with automatic shutdown systems in case of waste flow malfunctions. These controls can be either manual or automatic.

Temperature controllers are needed to regulate the temperature of incoming streams to the pretreatment section, reactor, distillation columns, and absorbers. Combustion temperature within the incinerator must also be monitored and controlled. Pressure must be controlled in the reactor and all of the columns. Pressure drops across the pollution control system and across the various process units should be measured and controlled. Flow rates must be measured and recorded for all waste streams. Flow rates could be measured by an orifice plate, sonic-type flowmeter, or rotameter. Flow rates should also be monitored and controlled downstream of any pumps and upstream of any flow control valves. Liquid feed to the incineration burner should be controlled to insure the correct mix of fuel and waste. Liquid levels in all storage and processing tanks should be measured and controlled to prevent overflow and to insure a free flow of fluid throughout the process. Either gauge glasses or automatic sensors could be used.

4.3.1.4 Effluent Monitoring--

Waste gases containing Cl_2 and HCl must be removed in an absorption unit. Effluent monitoring should be able to detect potential environmental pollutants. Ambient air samplers should be used to monitor all waste gas streams. Waste gas samples should be collected periodically for analysis. If incineration is used to eliminate chlorine residues, then government regulations specify that stack components must be monitored and sampled at specific intervals. It is preferable that monitoring during incineration be conducted by collecting and analyzing samples from holding tanks eliminating the need for frequent grab samples.

Liquid PCB wastes should be monitored by real-time measurement of the bulk flow rate and automatic continuous recording. Standard devices are commercially available for this purpose. The PCB concentration should be determined by periodic sampling and analysis of the PCB waste feed.

Solid PCB wastes should be monitored by weighing loads and monitoring the loading over regular intervals of 15 minutes or less. Waste residue from the incinerator may be monitored by using a weight scale. The facility operator should keep a record of the total weight of residue.

The Regional Administration should have available a manual describing sampling methods for the various streams that must be monitored.

4.3.1.5 Waste Characterization--

4.3.1.5.1 Range of PCB concentration--The chlorinolysis process has not been adapted to handle PCBs as of yet.

4.3.1.5.2 Limitations on constituents--Chlorinolysis works best on chlorinated aliphatic compounds. The feed must be a liquid with most solid impurities removed before processing. The process works poorly for an aromatic content of greater than 5% calculated as benzene. Feed material containing phosphorous, nitrogen, sulfur, or toxic metals may not be appropriate for chlorinolysis. The water content of the feed stream should be less than 20 ppm.

4.3.2 Environmental Factors

4.3.2.1 Potential Impacts of Disposal Operation--

An environmental impact statement for a chlorinolysis plant has not been formally developed but would be part of an overall assessment necessary prior to construction. The primary environmental factors that must be considered are:

- Shipment and handling of the hazardous organochlorine wastes prior to chlorinolysis
- Control of the potential gas and liquid effluents after conversion
- Handling and storage of the final products.

4.3.2.2 Potential Impacts of Disposal of Process Wastes--

Potential environmental dangers when considering the construction and operation of a chlorinolysis plant include the sudden occurrence of carbon tetrachloride in rivers and municipal water supplies and possible escape of phosgene, HCl, CO, and carbonyl chloride gas into the atmosphere. There are no data available describing emission of particulate matter from the chlorinolysis process. Such material could be emitted from the incinerator, but the lack of data prevents a discussion of expected impacts. The use of a scrubber should keep these emissions fairly low. Since the waste effluent streams are mainly liquid, any solid emissions would be dissolved in the liquid effluent as suspended particles. The liquid effluents should be discharged to a municipal sewage system after treatment. Residual organic or trace element components would be contained in the sludges generated by the municipal waste treatment system. If these sludges are landfilled, the effects of contaminants deposited into the soil will depend on the type and porosity of the soil.

4.3.2.3 Potential Impacts of Accidents--

Emissions from manufacturing, storage, and transport of polychlorinated aromatics, and particularly PCBs are possible. Accidental spills and leaks of both solid and liquid wastes are the primary sources of accidents. Although leaching from sanitary landfills is theoretically possible, evidence shows that losses by this route are negligible. Leaching from certain soil surfaces such as sand and bedrock into groundwater supplies is a likely source of contamination. Contamination of soil by irrigation is possible if the water is taken from a contaminated source. Improper disposal of PCB and polychlorinated residues from this process appear to have the greatest potential for damage.

4.3.3 Economic Factors

Since chlorinolysis has not been directly applied to PCB disposal, a cost analysis cannot be presented at this time. Capital costs, operating costs and possible credits have been determined for a chlorolysis plant with a capacity to process 25,000 Mg/year of waste chlorohydrocarbons (Wilkinson, et al., 1978). It was determined that a 15% discounted cash flow rate of return on investment at a disposal cost of \$133/Mg could be realized. Operating and financial data are presented in Table 6.

The capital investment for facilities could be as high as \$27 million for a plant processing 25,000 Mg/year of organochlorine waste. In 1978, the cost to destroy chlorohydrocarbons was \$0.13/kg. This assumed the present market price of CCl_4 was \$300/Mg. (Wilkinson, et al., 1978).

It was also estimated in 1978 that about 90 to 95% of all CCl_4 produced was used in the production of F-11 and F-12 refrigerants and aerosols. The future markets of these chlorofluorocarbons are uncertain because of the chlorofluorocarbon/ozone depletion research findings. Because potential maintenance of the CCl_4 market is uncertain, operating costs could be the major issue in determining if the chlorinolysis process is a viable PCB disposal method.

Overall, it now appears that the chlorinolysis process if applied to PCB disposal would require a large capital investment and large operating costs. A high CCl_4 recovery option exists, with a potential return on investment.

4.3.4 Energy Factors

In 1978, it was estimated that a 25,000 Mg/year mixed vinyl chloride monomer chlorolysis processing plant would use 9.2×10^7 MJ of electricity at \$0.015/kw-hr, 52,000 Mg of steam at \$4/Mg and $1.48 \times 10^7 m^3$ of cooling water at $\$0.003/m^3$. Energy credits may be available if some or all of the heat content of the PCB waste can be recovered and used for steam production.

TABLE 6. OPERATING AND FINANCIAL DATA FOR A CHLORINOLYSIS FACILITY PROCESSING 25,000 MT/YR OF ORGANOCHLORINE WASTE (WILKINSON ET AL., 1978)

Category	Quantity
Process data	
Chlorine gas consumption	93,800 Mg/yr
Carbon tetrachloride produced	88,500 Mg/yr
Hydrogen chlorine produced	30,000 Mg/yr
Reactor temperature	973°K
Reactor pressure	20.2 MPa
Cost data	
Depreciable investment	$27,210,000
Working capital	4,708,000
Annual operating cost, including royalty	19,881,000
Revenue from CCl_4 and HCl	28,050,000
Unit disposal cost at 15% discounted cash flow rate of return (DCFRR)	$ 133.59/Mg

Assumptions:

Location - Gulf Coast area

CCl_4 selling price - $300/Mg

HCl selling price - $50/Mg

Depreciation - 10 yr straightline

Income tax rate - 50%

Feedstock - vinyl chloride monomer wastes

4.4 THE GOODYEAR PROCESS

4.4.1 Technical Factors

4.4.1.1 State of Technology--

The Goodyear process is well developed on laboratory level and has been scaled up. It can only be concluded from the available literature source that the Goodyear process is technically applicable at this time to handle pure Aroclors or mixture of Aroclors in the 50-500 ppm concentration range. It is claimed that significant amounts of material have been treated with sodium naphthalide reagent to reduce PCB content from 130 ppm to 10 ppm. The process has proven to be selective and can be performed on site in existing equipment.

4.4.1.2 System Design--

In general, the Goodyear process was developed to meet four design criteria:

- Adaptability for complete and selective conversion of PCBs to non-toxic products
- Capability of being performed on-site in existing equipment
- Capability of treating small or large volumes of PCB-contaminated fluids
- Low cost

Evaluation and analysis of the specific unit processes comprising the overall process is very difficult since scale up data are not available.

4.4.1.2.1 Pretreatment and feed--Types of pretreatment that may be necessary are:

- Appropriate PCB feed rate adjustments
- Preparation of the sodium naphthalide reagent
- Solvent purification
- Removal of toxic components such as trace metals or inert constituents

The PCB feed rate must be known in order to determine the overall destruction efficiency. The maximum PCB input rate must be determined to evaluate the complete feed system. The feed rate would have to be controlled automatically to insure against over or under consumption of PCB material. The PCB feed rate will have a tremendous effect on most other process variables.

The sodium naphthalide reagent must be prepared properly so the reaction can be carried out as planned. Particular attention must be paid to stoichiometry when preparing the reagent. The mole ratios of sodium naphthalide to chlorine must be maintained between 50-100 to remove 98% of the PCBs from a heat transfer oil containing 83 ppm PCB (Goodyear, 1980).

Addition of the naphthalene-tetrahydrofuran solvent is critical to the process, and must be done slowly with adequate mixing. An extremely reactive form of sodium must be prepared by heating pieces of sodium metal in the heat-transfer fluid under an inert atmosphere. Temperature must remain between 423-443^{0}K for 5-10 minutes. This reaction is extremely exothermic, and the solution must be cooled rapidly to ambient temperature while mixing.

The heat transfer fluid must be cleaned, and inerts or toxic components must be removed before addition to the reactor. Any contaminant that could react with the sodium naphthalide should be eliminated at this stage.

4.4.1.2.2 Processing--Evaluation of unit processes can only be carried out for the scaled-up process. Lack of data prohibits an assessment of each unit process now. Only general assumptions can be made at this time based on available literature.

The overall reaction proceeds rapidly at room temperature. An evaluation of this phase of the process should consider any possible vapor emissions and the possible formation of particulates. Any excessive exotherms or increases in temperatures should be noted in the evaluation.

If naphthalene and tetrahydrofuran are to be recovered, then an evaluation of the recovery method must be done. Vacuum stripping may be the most favorable method for recovering these components, so important variables such as pressures and heat duties must be determined.

Recovery of the reaction residue could be accomplished by vacuum distillation. Important parameters that would need to be assessed are temperatures, pressures, heat duties, and flow rates in and around the distillation column. The pot residues from this distillation must be analyzed to see if further processing is required.

Any other process information should also be compiled for evaluation by the EPA Regional Administrator.

4.4.1.2.3 Pollution Control--Upon scaleup, an evaluation of all generic effluent streams must be carried out. Vapor streams must be analyzed for trace PCB residues as well as for chlorinated compounds and other toxic substances. Appropriate pollution control equipment such as scrubbers, filters, precipitators, etc., will have to be installed depending on the nature of the pollutants. If monochloro-biphenyls are produced, then traces of these may be contained in the vapor phase. Research is needed to indicate whether this could occur. If a sufficient amount of low molecular weight PCBs can exit as vapor, then those processes that emit the PCBs should be sealed off, and the emitted gases should be treated. Alternatively, it may be possible to reduce the PCB feed rate so that emissions are acceptable.

Liquid effluent streams could contain dissolved solids and toxic material which could be harmful to the environment. Appropriate pollution control devices should be installed to eliminate these pollutants. Unreacted PCBs could exist in an effluent stream. Monitoring devices should be able to detect even trace residues of unreacted PCB.

4.4.1.2.4 Destruction efficiency--In the Goodyear study, a destruction efficiency of 92% was achieved. Significant amounts of material were treated with the sodium naphthalide reagent to reduce the PCB content from 130 ppm to 10 ppm. This is below the 50 ppm lower limit for PCB contamination. The 92% destruction efficiency still falls below those of Annex I incinerators or high efficiency boilers.

4.4.1.3 Process Controls

An evaluation of process controls should include temperature control, pressure control, flow rate control, and any other necessary controls to enable the process to operate efficiently and safely.

Temperature is an important variable which will affect the overall PCB destruction efficiency and reaction rate. The PCB reaction with the sodium napthalide reagent is highly exothermic and must be adequately controlled. Temperature sensing devices would need to be installed to indicate any extreme increases in temperature or heat intake. Any heat exchangers used in the process should be controlled to guard against unwarranted temperature deviations.

Pressure will need to be controlled in the reactor and in any other processing equipment where pressure drops could affect the performance of the system. Compressors, pumps, and any other accessory pressure equipment must be controlled sufficiently.

Flow rates of all streams must be monitored and controlled. Flow rate is a critical variable affecting the overall performance of the process. The feed stream may be the most critical of all the streams that will need to be controlled. The feed rate will depend on the amount of PCBs contained in the stream.

Likewise, all pretreatment equipment and pollution control equipment must contain adequate process control devices to regulate important operating variables. A detailed analysis of required process controls cannot be carried out at this time without scaleup operational data.

4.4.1.4 Effluent Monitoring

Lack of process information prohibits a detailed assessment of effluent monitoring demands for the Goodyear Process. Only general guidelines may be presented at this time.

The Regional Administrator will evaluate the capability of the facility operator to monitor all important process effluent streams. The facility operator must describe all important process streams so a decision can be made about which streams should be monitored and what type of monitor should be used. In general, gaseous streams should be monitored and sampled periodically for both PCBs and other chlorinated compounds. Waste gases are not expected to be of major importance in the Goodyear Process, so sampling and monitoring them should pose no problem.

Liquid effluent streams from all sources should be monitored for PCB content and for other toxic or hazardous components including dissolved solids. Plant data concerning the stream should be logged and kept for future reference. Tap sampling may be used for liquids in motion or static liquids in tanks or drums. Automated samplers should be used to increase the chance of collecting a representative sample.

Solid waste streams should be sampled by a grab technique. Analysis for PCB and residual chlorinated hydrocarbon content of these streams should be performed. The location of solid sampling locations should depend on the ability to collect a representative sample.

4.4.1.5 Waste Characterization--

4.4.1.5.1 Range of PCB concentration--The Goodyear Process seems best suited to handle heat transfer fluids with PCB concentrations in the range of 50-500 ppm. The process may also be able to handle transformer fluids with PCB content greater than 500 ppm. More research is needed to determine the maximum concentration of PCBs that the process can handle.

4.4.1.5.2 Limitations on constituents--PCB wastes containing excessive concentrations of toxic heavy metals or containing inert substances will require pretreatment prior to entering the reactor. The type of treatment will depend on the nature of the materials to be eliminated.

4.4.2 Environmental Factors

Because very little information exists on disposal of PCBs by the Goodyear Process, it is extremely difficult to estimate environmental impacts. Environmental factors must be researched in detail upon scaleup of this process.

4.4.2.1 Potential Impacts of Disposal Operation--

It appears that minimal environmental impacts would be expected from the Goodyear Process. Since the chlorinated biphenyl content can be lowered to 10 ppm, environmental damage does not appear likely. There is a possibility that PCBs could be released to the ambient air but their content should be small. Trace amounts of unreacted sodium metal, naphthalene, and tetrahydrofuran could be released in liquid effluent streams. The chance of this seems minimal, since recycling and reprocessing could be used to recover these substances for reuse.

4.4.2.2 Potential Impacts of Disposal of Process Wastes--

The bulk of residual PCBs would be expected to be contained in the processed heat transfer fluid. This fluid could be recycled or reused directly so there is no real impact from this waste. Lower weight chlorinated biphenyls may exit as vapor from various process steps, but their concentration should be 10 ppm or lower. If any auxiliary processes are used to eliminate PCB residues or volatile organics, such as incineration or wet air oxidation, the potential environmental impact will increase. The possibility of other toxic or harmful substances being eliminated in waste streams such as HCl, trace metals, and chlorinated compounds should be determined in the scaleup study. Overall, the potential impacts of the disposal operation on the environment appear to be low although a thorough assessment cannot be made without the appropriate data.

4.4.2.3 Potential Impacts of Accidents--

It is very difficult to predict the potential impacts of accidents at this time. A spill or release of PCBs from the Goodyear Process could possibly result in contamination of surface groundwater through seepage; contamination of land areas where humans, animals, or croplands are exposed; and contamination of areas that could create airborne movement of PCBs.

Leaks or spills of other materials such as naphthalene, tetrahydrofuran, sodium, and various byproducts could also cause some environmental damage. The extent of this possible damage must be assessed. Spill prevention and control procedures must be developed pursuant to EPA regulations. Because of the possible threat to the environment, the facility using the scaleup version of the Goodyear Process must address all aspects of accident prevention. The process should be evaluated according to EPA regulations covered in Section 2 of this report.

4.4.3 Economic Factors

The following quantities of materials were recommended for the reagent preparation and in the large scale treatment of a heat-transfer fluid contaminated with 82 ppm of chlorinated biphenyls. Quantities are given per 1 kg (2.2 lbs) of fluid to be treated. The prices quoted are given in the

"Chemical Marketing Reporter," April 2, 1979.

	kg	$/kg (2.2 lb)	$/100 kg (220 lbs)
Sodium Metal	0.05	1.41	0.155
Heat-Transfer Oil	0.50	-	-
Naphthalene	0.32	0.79	0.557
Tetrahydrofuran	0.89	1.89	3.69
			2.0025

No credit for the recovery of naphthalene or tetrahydrofuran was considered in developing these material costs. With large scale application of this process, product recovery may be economically feasible.

Generally, the Goodyear Process appears to be relatively low in cost and may be adaptable to both small or large scale operation. A detailed economic evaluation will need to be performed before this process may be judged economically justified.

4.4.4 Energy Factors

Available information from the Goodyear Tire and Rubber Company did not include any data about energy requirements. The amount of energy required per unit weight of PCB converted must be determined in the overall assessment. It should be determined whether some or all of the heat content of the PCB waste may be recovered to produce steam for an energy credit. Further assessment of energy factors cannot be carried out at this time. However, the Goodyear Process does not appear to consume a large amount of energy per unit weight of PCB converted.

4.5 MICROWAVE PLASMA

4.5.1 Technical Factors

4.5.1.1 State of Technology--

A 15 kW microwave plasma reactor system capable of destroying 2 to 11 kg per hour of organic wastes including PCBs is now in operation.

4.5.1.2. System Design--

4.5.1.2.1 Pretreatment and feed--Special operations are necessary for dispensing the feed into the reaction zone. Gases and volatile liquids must be handled differently. The feed must be dispensed from its reservoir at atmospheric pressure or greater into a reduced pressure environment of about

6,000 Pa. Reduced pressure in the plasma reactor can be used to pull the liquid through a needle valve below the reservoir. Liquid feed can also be introduced by using a peristaltic pump that controls the flow of liquid. The feed must uniformly fill the reactor cross section. The liquid must either be dispensed directly to the plasma or can be flashed to vapor before delivery to the plasma. The throughputs of the reactor will be limited by the feed system and not by the plasma's ability to detoxify the reactant. Constituents that could cause corrosion or interfere with the microwave processes must be removed before entrance into the reactor. Conventional pretreatment systems such as filtration, evaporation, absorption, etc., could be used.

4.5.1.2.2 Processing--Reactor design is of critical importance. The reactor tube must have the proper dimensions to prevent leakage of the microwaves out of the applicator where the reactor tube enters and exits. The reactor tube must be in a vertical position to allow liquid feed to flow directly into the plasma without contacting the walls of the tube. Thermal degradation or charring could occur in this zone if the liquid is allowed to contact the walls of the tube. If a nonvertical reactor must be used, a jet or nozzle should be used to squirt the liquid feed into the reactor. The reactor must be transparent to avoid overheating by absorption of microwave energy and must have high thermal shock resistance to avoid breakage when 15 kW of microwaves suddenly heat the packings or gases to high temperatures. It is also critical that the reactor tube be transparent to infrared and visible radiation to allow for radiative cooling of the hot gases and packings. Attention must be paid to construction materials. Material that will not shatter when heated rapidly in the microwave fields must be used. In several reactor designs, quartz was found to be the only material capable of withstanding the severe conditions in the plasma. Critical process parameters are: microwave power density, plasma length, PCB feed rate, and oxygen/PCB ratio.

4.5.1.2.3 Pollution control--The effluent gases leaving the plasma are extremely hot, corrosive and will contain large amounts of chlorine. The effluents will need to be treated to lower the temperature and to remove acid products. Radiative heat exchangers should be used to cool the process effluents. Acid products must be removed in a caustic scrubber. The caustic will have to be replaced periodically as it is consumed by the reactions with the acids.

4.5.1.2.4 Destruction efficiency--It has been determined on a laboratory scale that the destruction efficiencies of Aroclor 1242 and Aroclor 1254 are 99%, using 4.6 and 4.5 kW microwave power respectively. (Hertzler et al, 1979).

4.5.1.3 Process Controls--

The process control system for a 15 kW microwave plasma reactor system is extremely complex. The cooling water required by the microwave power supplies must be automatically turned on whenever the microwave control circuits are turned on. An induced draft fan must be used to pull cooling air through the microwave power application and around the quartz reactor tube. Pressure in the reactor must be regulated. If the pressure rises too high, the oxygen flow, the reactant feeder, and the microwave power output would be shut off. If the plasma were extinguished while the microwave power were being applied to the reactor, the oxygen flow and the reactant feed would be shut off. A low pressure switch should be activated if the caustic recirculation pump on the caustic scrubber fails. This will shut off the fan on the scrubber, and, as a consequence, the pilot tube sensor on the scrubber inlet would sense the loss and activate an annunciator.

4.5.1.4 Effluent Monitoring--

The effluent gases leaving the plasmas are hot (up to 2000^{0}K), corrosive (often containing large amounts of chlorine), and under a vacuum. Monitoring will be required to lower the temperature and remove acid products from the gases. Process effluents exiting the plasma must be cooled and then compressed to atmospheric pressure. It is important that the proper types of heat exchangers and vacuum pumps be used for this process. Traditional rotary oil-seal vacuum pumps would very quickly become contaminated with acid products and clogged with water condensed during the compression.

The caustic scrubber on the vacuum pump exhaust removes acid products by passing the gases through a bed sprayed with caustic. Caustic is lost by reactions with the acids and must be monitored and replaced.

The amount of any residual reactant leaving the plasma should be monitored for and analyzed. Gases leaving the plasma should be sampled by using conventional methods based on drawing the gas through a tube packed with adsorbent that collects the components of interest.

It must be remembered that the purpose of effluent monitoring is to determine the extent of PCB degradation and to assess the potential environmental impacts of undestroyed PCBs and any other toxic or hazardous material contained in the effluent stream. To meet this requirement, careful effluent monitoring at all important entrance and exit points to process equipment should be applied.

4.5.1.5 Waste Characterization--

4.5.1.5.1 Range of PCB concentration--The process should be able to handle PCB concentrations within the 50-500 ppm range effectively. Further, research needs to be done to determine the maximum concentration of PCBs that can be destroyed with a high destruction efficiency.

4.5.1.5.2 Limitations on constituents--Any constituent that will interfere with the microwave process or that could cause extreme corrosion of reactor equipment should be eliminated. It is important to note that as the number of chlorine atoms on the PCB molecule increases, the destruction efficiency decreases.

4.5.2 Environmental Factors

4.5.2.1 Potential Impacts of Disposal Operation--

An environmental assay of the disposal operation must consider: the shipment and handling of the PCB prior to processing, control of the potential gas and liquid effluents after conversion, and handling and storage of the final products. Possible leaks from the caustic scrubber system must be controlled.

4.5.2.2 Potential Impacts of Disposal of Process Wastes

Though microwave plasma degradation is a controllable method which yields innocuous products like CO_2 and H_2O. Potentially hazardous products like CO, and chlorides will also be produced. The Cl_2 could possibly show up in rivers and municipal water systems. Particulate matter emissions do not appear to pose any significant threat to the environment. The use of a caustic scrubber should keep emissions fairly low. Since the waste effluent streams are mainly liquid, any solid emissions would be dissolved in the liquid effluent as suspended particles. The liquid effluents should be discharged to a municipal sewage system after treatment. Any contaminants from the scrubber process would be contained in the sludges generated by the municipal waste treatment system.

4.5.2.3 Potential Impacts of Accidents--

To insure safe operation of the plasma microwave reactor system, a series of interacting safety circuits that automatically shut off the unit or warn the operators if certain process parameters are not in the safe range should be installed. These should include the following:

- If the water flow rate to the water ring seal vacuum pump is insufficient, it should activate an annunciator.
- If the temperature of the gases entering the shell and tube heat exchanger approach the critical temperature where the heat exchanger coating could be damaged, an annunciator should be activated to warn the operators.

Extremely high temperatures and pressures occur throughout the system. The potential for accidents should be an important variable entering into the process design. Accidental spills and leaks of both solid and liquid wastes could be the primary source of accidents. These spills and leaks could be minimized by conventional prevention methods.

4.5.3 Economic Factors

Very little information exists on the economics of a microwave plasma process adapted to PCB detoxification. The apparatus has a potential advantage of being made into a mobile unit, with a relatively low initial cost. The following calculations will need to be made in estimating the net profit per kilogram of PCB destroyed by the microwave plasma unit:

- Electrical costs
- Liquid oxygen costs
- Steam costs
- Labor costs
- Available credits from recoverable products
- Capital costs.

Overall capital costs for PCB detoxification may be high since useful byproducts may not be recoverable. A rough cost of $0.44/kg of PCB processed has been determined for oxygen and steam plasmas. (Wilkinson, et al., 1978) in 1978. Electrical costs should decrease as microwave power technology advances. Improvements in basic plasma design should cut operating costs substantially. Overall cost for a mobile unit will also depend in part on the distance to the user's site and the concentration of PCBs to be removed from the heat transfer material. At this time, it appears that a large scale microwave plasma detoxification unit will moderate capital investment and operating costs.

4.5.4 Energy Factors

A detailed literature search uncovered very little information about the energy requirements of this process. Since microwave plasma destruction uses energy from free radical reactions rather than energy derived from heat or molecular motion, the entire reaction zone may operate just slightly above room temperature. This may lower the energy costs slightly and is an important factor to consider when evaluating the energy efficiency of the process. Large amounts of energy may be needed to drive the microwave reactions, so the energy demand for this process must be examined very carefully. The possibility of recovering waste heat for steam production should be assessed, as this could provide a substantial energy credit.

4.6 OZONATION PROCESSES

4.6.1 Technical Factors

4.6.1.1 State of Technology--

UV-Ozonolysis has proved to be an effective method for the destruction of PCBs in industrial waste water on the laboratory level only. Scaleup to pilot plant level has not been attempted.

4.6.1.2 System Design--

4.6.1.2.1 Pretreatment and feed--Untreated water samples containing PCBs will also contain other components in trace amounts that could react with the UV radiation and with the ozone. Precautions must be taken to eliminate as many of these constituents as possible. Filtration, evaporation, carbon adsorption, or any other suitable pretreatment method should be used to eliminate these contaminants before exposure to the UV radiation and ozone.

4.6.1.2.2 Processing--Important operating variables include: ozone flow rate, ozone concentration, UV intensity, and residence time. Batch tests need to be carried out to determine the effect of each one of these variables on the degree of destruction of the PCB molecule. Batch tests are also needed to determine the UV-ozone reactor size, the ozone generator output requirements, and the affect of UV light on the rate of oxidation. Reaction conditions should be varied to determine the utility of this method to destroy PCBs. Oxone is produced from liquid oxygen in an ozone generator. The reactor will emit gases which should be passed through a thermal decomposer to break down the ozone before being discharged. It is extremely important to provide an effective heat transfer surface for the ozone in the thermal decomposer. Since ozone decomposes above $440^{\circ}K$, temperatures above this must be generated. The thermal decomposer must be made of stainless steel and packed with stainless steel wool. Ozone is extremely corrosive, so care must be taken to use proper material in all the processing equipment that the ozone will contact. PCBs have an extremely low vapor pressure, and would not be expected to evaporate quickly. Their low solubility in water will make them fairly susceptible to removal by sparging.

4.6.1.2.3 Pollution control--Pollution control devices must be installed to monitor and rectify gases given off from the reactor. These gases may contain some ozone, CO_2, CO, and possibly some simple chlorinated species. The UV-ozone reactions need to be studied further to determine the exact nature of the wastes given off so adequate pollution control devices can be installed.

4.6.1.2.4 Destruction efficiency--The destruction efficiency is defined as:

$$DE = 100 \left(\frac{PCB_{in} - PCB_{out}}{PCB_{in}}\right)$$

Substituting values from one of the experiments carried out by General Electric Corp. gives a destruction efficiency of approximately 93% ± 3%.

It is important to note that the PCB concentrations were in ppb.

4.6.1.3 Process Controls--

Temperature, pressure, flow rate, liquid level, and pH must be monitored and controlled throughout this process. In order to achieve the required degree of process control, these variables must be defined completely. Suitable controllers must be chosen to manipulate these variables. The temperature in the reactor must be controlled for the reaction to proceed properly. Pressure must be controlled in the ozone generator. All flow rates to and from the reactor must be monitored and controlled to insure the correct stoichiometric amounts of reactants. The liquid level in the reactor must be controlled to guard against overflow. The reaction solution must also be at the proper pH. Ozonolysis can only occur within a specific pH range, so it is vital that pH should be controlled.

4.6.1.4 Effluent Monitoring--

Because UV-ozonolysis appears to be best suited for removing PCBs from dilute aqueous streams, effluent monitoring should be conventional in nature. Extensive routine monitoring for water quality parameters should be taken in order to determine the composition of all waste water streams. Gaseous emissions of PCBs would best be sampled by using high volume ambient air samplers modified with polyurethane foam as an adsorbent (Stratton, et al., 1978). All the air sampling instruments used should have a high demonstrated efficiency under field conditions. The monitoring instruments should be able to detect very dilute amounts of ozone carbon monoxide, and simple chlorinated species. Conventional monitoring devices such as chromatographs and spectrometers could be used to help regulate effluent composition. If a scrubber is used to eliminate chlorinated compounds such as HCl, its effluent should be monitored for trace quantities of hazardous materials. The operator of the facility should list and describe the various streams that will need to be sampled. Tap sampling should be used to monitor flowing liquids and liquids in tanks or drums.

4.6.1.5 Waste Characterization--

4.6.1.5.1 Range of PCB concentration--PCB concentrations handled by the various laboratory processes have ranged from 30 ppb to 100 ppb in aqueous solution.

4.6.1.5.2 Limitations on constituents--Any material that could interfere with the UV-ozonolysis process should either be eliminated or minimized. Many contaminants will not react with UV radiation. Some of these may prove to be toxic would be introduced into the atmosphere along with the vent gases. Alternatively, some constituents could react with the UV radiation and ozone to create undesirable products. Because of this, the wastewater feed should be limited to only those constituents that can safely react with the ozone and UV radiation. More research is needed to determine the limitations on constituents to such a system.

4.6.2 Environmental Factors

4.6.2.1 Potential Impacts of Disposal Operations--

Shipment and handling of the PCB wastes prior to UV-ozonolysis must be included in an environmental evaluation. The process facility might not be located on the same site where the PCB wastes are produced. An assessment of shipping risks and handling procedures should be carried out. Methods for handling and storage of the final products must also be carried out. Some of the products might be toxic or corrosive. An assessment of types of final products that will be produced as well as equipment necessary to handle them will be necessary. Any auxiliary disposal operations such as adsorption, filtration,or incineration, must be analyzed for possible environmental damage.

4.6.2.2 Potential Impacts of Disposal of Process Wastes--

The possibility of reaction products being formed which are harmful to aquatic life must be considered. Residual amounts of halogenated compounds as well as trace metals may be contained in the waste effluents. These products could possibly accumulate in aquatic organisms. Vent gases may also contain toxic or harmful substances. Various chlorinated compounds as well as other toxic substances could accumulate either in the atmosphere or on land.

4.6.2.3 Potential Impacts of Accidents--

Accidental spills and leaks of both solid and liquid wastes are the primary sources of accidents. Precaution against UV radiation and ozone leaks must be taken. Implementation of available control technology will make it possible to minimize PCB loss during transfer, storage, and disposal. A spill or release of PCBs from a UV-ozonolysis facility may pose the following threats:

- Contamination of surface or groundwater
- Contamination of land areas where humans, animals or croplands are exposed
- Contamination of areas that could lead to significant airborne movement of PCBs.

As noted in Section 2.1, regulations pursuant to the Clean Water Act currently require facilities disposing of PCBs to prepare spill prevention control and countermeasures plans. These plans should detail safe handling procedures for hazardous materials including PCBs. They also should address prevention and control procedures when a release of PCBs occurs. An adequate SPCC plan should minimize the potential for spills, and therefore potential environmental impacts should be reduced.

4.6.3 Economic Factors

A large scale "Ultrox" UV-ozone processing plant is now operating at the Iowa Ammunition Plant in Brislington, Iowa. Approximate costs have been determined and are as follows:

Maximum capacity	567 m^3/day
Average output	567 m^3/day
Lease term	3 years
Installation	\$12,000
Annual Lease	\$87,359
Additional Charges	\$32,820
Power and Labor	\$52,260
Total Operating Cost per year	\$172,439
Treatment cost per m^3 (264.5 gal)	\$ 0.87

These costs were determined in 1979 and will need to be adjusted to current rates. Principal capital equipment costs will be the reactor, ozone generator and power supply, and the UV irradiation source and power supply. Principal operating costs include electrical energy and labor. In general, UV-ozonolysis should be cost competitive if applied to dilute aqueous PCB solutions on a large scale. An economic analysis should also consider whether or not it is possible to obtain credit for products or by-products. Expected costs of closure and post closure monitoring and maintenance should also be determined.

4.6.4 Energy Factors

The amount of energy required per unit weight of PCB waste destroyed is a critical factor in determining whether or not the process is viable. An extensive literature search could not uncover any information dealing with energy requirements for UV ozonolysis. An assessment must be made to determine overall energy debits and credits, such as the possibility of reclaiming the heat content of the PCB waste to produce steam.

4.7 PHOTOLYTIC PROCESSES

4.7.1 Technical Factors

4.7.1.1 State of Technology--

Photochemical destruction of organic material has not been applied on a large scale, and has rarely been directly applied to the degradation of PCBs. Success has been achieved in the laboratory with various classes of dioxins and other toxic pesticides.

4.7.1.2 System Design--

Because photolytic processes have rarely been applied to PCB degradation and are on the laboratory scale only, a direct analysis of the technical factors affecting system design is very difficult. Only assumptions can be made at this time. Important questions that must be considered for the overall system design include:

- How rapidly do photochemical reactions occur?
- What energy input is necessary?
- What products will be formed, and how are these products affected by the physical state of the reactants?

4.7.1.2.1 Pretreatment and feed--Laboratory research studies have used mono-, di-, tri-, and tetrachlorinated biphenyls in the photolysis studies. The PCBs have been purified by recrystallization from ethanol. Industrial scale up would require adequate pretreatment to eliminate any material from the feed stream which could interfere with the photochemical reactions. Contaminants that could lower the solubility of the PCBs would also need to be removed by a suitable pretreatment process.

Currently, photolysis has not been tried on a PCB-contaminated transformer or capacitor fluid. The effect of the numerous PCB isomers on the degradation process needs to be investigated to determine limiting feed characteristics such as composition and flow rates.

4.7.1.2.2 Processing--Intensive studies need to be carried out to determine how useful ultraviolet radiation is in decomposing PCBs. The rupture of a chemical bond requires a certain amount of energy. The dissociation of a carbon-carbon bond requires an input of about 418.4 kJ/mol. Light possessing at least this amount of energy must be used. The source must provide a reasonable amount of energy at low wavelengths. A medium pressure mercury arc lamp meets this requirement. Its maximum energy distribution is around 254 nm. It is important that the lamp be contained in a quartz housing to allow the passage of lower wavelengths. If photolysis is to occur at all, the PCB molecule must first absorb light energy above 290 nm or receive energy from another molecule through an energy transfer process. A study of the process must try to determine the structure of the resulting photoproducts, the effects of solvents on product formation, reaction rates, and the relationships between PCB structure and the rate of photolysis. The three most important processing variables which must be controlled are: a hydrogen-donating solvent must be present, UV light of the correct wavelength must strike the solution properly, and this light must be absorbed. Choice of solvents is also a critical factor. The PCB material must be in liquid form, so any solid material must be put into solution. Photochemical studies of PCB degradation are minimal. The emphasis has been on irradiating the PCB material at 300 nm in different solvents such as methanol and hexane for different time periods. The photoproducts are analyzed, and mechanistic pathways are theorized. Not all process parameters needed to establish photolysis as a viable process for PCB degradation have been defined, and any discussion of them would be purely speculative.

4.7.1.2.3 Pollution control--Intensive studies need to be carried out to determine the final products, including by products and residuals, before the question of pollution control can be addressed. The effluents resulting from photodecomposition may be complex mixtures containing toxic and corrosive compounds. The current data base prohibits even a qualitative assessment of what types of control devices would be necessary for pollution control. Typical pollution control equipment such as scrubbers and adsorption towers would not be easily adaptable to the photolysis process if adverse pollution effects are found to occur.

4.7.1.2.4 Destruction efficiency--Destruction efficiencies as such have not been determined for the laboratory PCB reactions. A 90-95 percent yield of dechlorinated PCB in methanol solution has been determined in the experiments done by Ruzo (Ruzo, et al., 1974). Methanol substitution products were also found in these experiments.

4.7.1.3 Process Controls--

Elaborate process controls would be necessary to control flow rates, temperatures, pressures, and UV intensity upon scale up. Flow rates of all incoming the outgoing streams would need to be monitored and controlled. Temperature in the reactor must be controlled to provide adequate reaction conditions. Pressure drops through any process equipment such as heat exchangers, compressors, or pumps must be controlled. Only UV radiation of certain wavelengths should be allowed to penetrate the reaction solution. This can be controlled by using the proper UV light source along with appropriate filters. Safety control circuits regulation the UV power supply would have to be installed to insure against over exposure of the reaction solution to the UV radiation. The specific types of controllers and where they should be located in the process scheme cannot be predicted until scale up studies are done.

4.7.1.4 Effluent Monitoring--

As stated earlier, photolysis used as a destruction method for PCBs has barely been researched at this time. The breakdown and analysis of all possible effluent waste streams has not been done. Since the effluents from this process could be complex mixtures of extremely toxic and corrosive compounds, an assessment of the types and locations of monitoring devices would be an integral part of scale up operations. Careful effluent monitoring will be needed to determine the extent of PCB conversion and to determine the potential environmental impacts of any undestroyed PCBs or any other hazardous material.

Liquid effluent streams must be monitored for PCB content and for the occurrence of HCl and other chlorinated compounds. Periodic samples from all waste streams should be analyzed for content in a laboratory. Any vent gases should be monitored by using ambient air samplers. Periodic air samples must be collected and analyzed for PCB content and overall composition.

The effluent monitoring capability of a photolysis treatment facility is determined by the facility operators' description of the appropriate streams to be sampled. Prior to sampling any effluent stream, plant data concerning that stream must be available. Overall, effluent monitoring should be automated. Units are readily available and capable of monitoring the complex effluents generated by the photolysis process.

A data base must be developed before a detailed assessment of viable effluent monitoring schemes can be developed.

4.7.1.5 Waste Characterization--

4.7.1.5.1 Range of PCB concentration--The photolysis process may be applicable over a wide range of PCB concentrations. The process should work for dilute solutions as well as for PCB concentrations greater than 500 ppm. The important factor determining the concentration range of the PCBs is its solubility in the solvent. Research has not been done on an actual PCB mineral oil, so the applicability of this process to the real life situation is not completely validated.

4.7.1.5.2 Limitations on constituents--Any component in the feed stream which could react with the PCBs and UV radiation should be eliminated by pretreatment. Particulate matter and nondissolvable solids should either be eliminated or reduced by pretreatment. Any constituent that could cause corrosion or fouling of any of the process equipment must be removed. Presently, it is not known which substances could interfere with the photolysis process.

4.7.2 Environmental Factors

4.7.2.1 Potential Impacts of Disposal Operation--

The overall disposal operation is underdeveloped. Basic environmental impacts must be outlined before an empirical assessment of the disposal operation can be determined. Possible hazards will include the shipment and handling of the PCBs prior to photolysis, control of the potential gas and liquid effluents after conversion, and handling and storage of the final products. Each one of these areas must be researched in the environmental assessment. Shipment and handling of the PCBs do not pose any real risks if appropriate safety regulations are followed. Control of the various effluents will depend on the nature of the effluents. Research is needed to determine the possible composition of each stream in the process so the overall impacts from the disposal operation can be determined. Handling and storage of the final products can be accomplished safely by using standard safety precautions.

4.7.2.2 Potential Impacts of Disposal of Process Wastes--

The precise chemical nature of the process wastes will need to be investigated heavily before assumptions about process waste disposal can be made. Progress in identifying all the possible side products of PCB photolysis has been extremely slow. Because the mineral oil may contain numerous isomers of the PCB molecule, process waste characterization is very difficult. Certain chlorinated compounds may exist in the waste streams that could be harmful to the environment. Gaseous effluents could contain hydrochloric acid and photoactive compounds. Aqueous effluents could contain chlorine and possible components that did not react with the UV radiation. These substances could react further, creating either toxic or inert compounds which could cause environmental damage.

4.7.2.3 Potential Impacts of Accidents--

Accidental spills and leaks of solid, liquid, and gaseous wastes are the primary sources of accidents. These can be minimized by standard preventive procedures. Solid wastes may contain toxic substances that could percolate into the soil and have damaging effects on irrigation and water consumption sources. Liquid wastes may contain dissolved solids and toxic substances that could cause problems for aquatic or marine organisms. Aquatic toxicity tests will be required to determine the impact of aqueous wastes on aquatic and marine organisms. Overall, the potential for accidents will need to be assessed upon scale up, since laboratory studies alone cannot forecast possible emergency situations that could occur in an industrial situation.

4.7.3 Economic Factors

To date, the economic impacts of the large scale application of photolysis have not been determined. Some of the factors that will affect overall capital and operating costs include: land availability and cost, types of chemicals and reagents required, labor, monitoring, application costs, etc. Photolytic degradation of PCBs must be researched further in both laboratory and field studies before an economic evaluation of this technology can be carried out. Based on the limited information available, scaled up operating and capital costs appear to be moderate. Possible economic credits could be gotten if some of the products are saleable or reuseable. This must be determined in further laboratory studies.

4.7.4 Energy Factors

Because photolytic degradation of PCBs has barely been researched in the laboratory and has not been applied on an industrial scale, energy usage cannot be determined. The amount of energy consumed per unit weight of PCB destroyed will need to be determined as an energy debit. Energy credits may be earned if some or all of the heat content of the PCB waste can be recycled to produce steam.

4.8 REACTION OF PCBs WITH SODIUM, OXYGEN, AND POLYETHYLENE GLYCOLS

4.8.1 Technical Factors

4.8.1.1 State of Technology--

The use of molten sodium metal dispersed in polyethylene glycols to degrade PCBs has been accomplished effectively on the laboratory scale only.

4.8.1.2 System Design--

4.8.1.2.1 Pretreatment and feed--Components in the feed stream that could interfere with the main reaction between the PCB oil and the molten sodium metal must be removed by appropriate pretreatment processes. The reaction is highly exothermic so any contaminants that could cause extreme temperature variations or side products should be eliminated prior to processing. Constituents that could decrease the solubility of the PCB oil in the solvent should also be removed or degraded by pretreatment.

4.8.1.2.2 Processing--Important process variables need to be defined before scale up is attempted. Particular attention must be paid to temperatures and stoichiometry. The temperature in the reaction vessel must be raised above the melting point of the metallic sodium (370.28°K). Adequate mixing of the reaction mixture of polyethylene glycol and PCB oil must be achieved to provide a uniform dispersion. Cyclohexane or any other appropriate solvent must be used to extract the organic components out of the solution. The melting of the sodium in the polyethylene glycol must be done in an oxygen free environment. When air is later allowed into the system, a vigorous, exothermic reaction will occur. A large amount of hydrogen gas will be emitted. It is important to note that only in the presence of oxygen will the molten sodium react with all the glycolic solvents. Dechlorination will not occur in nonpolar low volatility liquids, in glycolic solvents where both terminal hydroxyl groups are replaced with alkoxy groups, or in glycols in the absence of air.

4.8.1.2.3 Pollution control--Large amounts of NaCl and hydrogen gas will be evolved in this process. The hydrogen gas must be drawn off and could be collected as a valuable source of energy. Also, with scale up, the large quantities of NaCl produced would not create any special disposal problems. The recovered hydrogen gas could be used as an additional source of energy to melt the NaCl. Containment and removal of any other residual wastes should be an important consideration in scale up studies. Appropriate pollution control equipment would have to be installed to meet government regulations. Any waste gases would have to be either removed in an absorption unit, by any other appropriate method, or recycled for reuse. Further laboratory studies are needed to determine the precise composition of the waste gases.

4.8.1.2.4 Destruction efficiency--Laboratory studies have indicated an approximate 95 percent conversion of the PCB oil. Precise destruction efficiencies have not been determined.

4.8.1.3 Process Controls--

Upon scale up, emphasis must be put on process control. Extreme heat is generated by the addition of the sodium metal. This heat must be monitored and controlled with appropriate temperature controllers. Various types of control circuits may have to be installed for both safety and monitoring purposes. Flow rates of any waste gases, particularly hydrogen, must be regulated. Flow rates of each stream should be monitored and adjusted to meet process conditions. It is extremely important that the pressure in the reactor and any other processing equipment be maintained within the optimum operating range. Pressure valves and controllers must be installed to control pressure drops through the heating elements and to control abnormal pressure deviations. Liquid levels in the reactor and storage tanks must be monitored for overflow and to insure a free flow throughout the process.

4.8.1.4 Effluent Monitoring--

As stated earlier, the reaction of molten sodium with polyethylene glycols will produce large amounts of hydrogen gas. It is critical that the precise amount of gas evolved be determined so appropriate safety devices should be placed at strategic locations to monitor critical paramters such as temperatures, pressures, and flow rates. Ambient air samplers can be used to monitor the hydrogen and any other evolved gases. Effluent streams which contain the polyhydroxylated biphenyls must also be monitored. These compounds may prove to be toxic to humans or animals in the immediate vicinity of the processing facility. Streams containing NaCl should also be monitored for the existence of dissolved solids and possible toxic compounds. Though effluent monitoring is important, it is possible that the recovered hydrogen gas could be used as a source of energy to melt the NaCl and, using electrolysis techniques, reduce it to sodium metal and chlorine gas. This process would decrease the importance of monitoring although recycling would have to be carefully engineered.

Liquid effluent streams must be monitored for PCB content and for the existence of HCl and other simple chlorinated compounds. Standard monitoring devices may be used to examine periodic samples from each effluent stream. A careful analysis of all effluent streams must be carried out if this process is to be commercialized.

4.8.1.5 Waste Characterization--

4.8.1.5.1 Range of PCB concentrations--The process appears to be applicable over a wide range of PCB concentrations, particularly in the range from 50-500 ppm. The process could also be effective for concentrations greater than 500 ppm.

4.8.1.5.2 Limitations on constituents--Any constituent that will either interfere with the molten sodium reaction or that will decrease the solubility of the PCBs should be eliminated before processing by appropriate pretreatment.

4.8.2 Environmental Factors

4.8.2.1 Potential Impacts of Disposal Operation--

Potential hazards from the disposal operations are hydrogen gas leaks and storage and handling of the hydrogen gas and any residual PCBs. Hydrogen gas is highly flammable and common sense safety measures should be used to avoid costly accidents when reprocessing it. Transportation and storage of the PCBs can pose impacts. Standard preventive procedures should be used to prevent leaks and spills, both before and during processing.

4.8.2.2 Potential Impacts of Disposal of Process Wastes--

Direct disposal of NaCl does not pose any serious problems. The large quantity of hydrogen gas evolved should be recovered and reused as a source of energy to melt the NaCl. The hydrogen gas could possibly be used to reproduce the sodium metal by using electrolysis techniques. This could result in a recycling of the sodium metal and chlorine gas. Polyhydroxylated biphenyls are also produced by the reaction. These are useful compounds that could be sold and used as antioxidants in foods or in the preparation of various types of polymers.

4.8.2.3 Potential Impacts of Accidents--

The evolution of large amounts of hydrogen gas means that the use of open flames, electrical sparking, and electric heating elements must be avoided. The reaction with the sodium metal should be started with heat supplied by steam. Since the reaction with sodium metal is extremely exothermic, heat must be continuously removed from the reaction vessel. Caution must be taken to insure against extreme temperature rises in the reactor. Improper handling of the PCBs during shipping and storage could cause serious accidents. Established safety methods should be applied to the shipping and storage phases of this process.

4.8.3 Economic Factors

Franklin Research Center engineers determined a preliminary cost evaluation for the commercial destruction of PCBs by the sodium-polyethylene glycol process (Pytlewski et al.,1980). Assumptions made were the following:

- Construction of a complete disposal facility
- Na metal currently selling for 90¢/kg
- Polyethylene glycol 400 selling for 84¢/kg

They determined a cost of decomposition of about 70¢/kg of PCBs. Because of wide fluctuations in the price of metallic sodium, it was determined that the low side of the cost estimate could reach 22¢/kg of PCBs. Possible credits could be obtained from the recovery of hydrogen gas and the polyhydroxylated biphenyls which could be used as polymers, antioxidants, and solvents for high temperature reactions. These credits could bring the cost of the operation low enough, making the process profitable. It is not possible to perform a detailed cost analysis of this process at this time. The economic feasibility of this process will need to be determined before scale up operations can start.

4.8.4 Energy Factors

The amount of energy needed per unit weight of PCB destroyed must be determined as an integral part of the overall economic assessment of this process. This could turn out to be a fairly high percentage of the operating cost. On a large scale, hydrogen gas could be drawn off and reused as a valuable source of energy. As stated earlier, it is also possible that the recycled hydrogen gas could be used as a source of energy to melt the NaCl, though the cost of this method will need to be determined. Because of a technical information gap, the overall energy effectiveness of this process cannot be determined at this time, and an intensive energy study will need to be carried out to determine all possible energy credits and debits.

4.9 THE SUNOHIO PROCESS

4.9.1 Technical Factors

Limited data are available at this time pertaining to the fully operational mobile unit. A demonstration was performed on October 23 for the EPA. Results and detailed process parameters do not exist in the literature currently. The following treatment is based upon generalized, nonconfidential information received from Sunohio. (Sunohio, 1980).

4.9.1.1 State of Technology--

It is stated that an operational mobile unit now exists which can destroy PCBs in transformer oil after pretreatment consisting of filtration and removal of acids and other contaminants. The mobile unit will remove and destroy all PCBs contained in the transformer oil and will leave the oil in reusable condition. The process is also capable of destroying pure PCBs.

4.9.1.2 System Design--

All the necessary process equipment is contained in a large mobile tractor-trailer. The equipment is self-contained and can either generate its own power or operate from an external electrical power source. Precise system design parameters are not available from Sunohio at this time. A detailed evaluation of the overall system design must include an analysis of the various unit processes. A possible evaluation scheme could be organized as follows:

- Evaluation of the feed and pretreatment system, including such processes as washing, filtration, and conventional oil treating methods

- Evaluation of the reaction and processing scheme including reactor design parameters
- Evaluation of pollution control and effluent handling systems. Product evaluation and process control methods should be included.
- Evaluation of all auxiliary equipment such as heat exchangers, compressors, pumps, etc.

The transformer oil should be traced through the system, and all relevant design parameters should be compiled and assessed.

4.9.1.2.1 Pretreatment and feed--The pretreatment process will consist of filtering the heat transfer oil and removing moisture, acids, and other contaminants from it. Other conventional oil treatment processes may be needed for pretreatment. Feed composition should be monitored, and feed rates need to be controlled. Injection devices, pumps, and heaters should be adequately controlled to maintain constant flow rates and temperature for the incoming streams. A gas chromatograph or any other suitable detection device should be used to analyze the incoming feed stream. The pretreatment evaluation should include an analysis of the vacuum degasser, which is used to elevate the temperature of the oil before starting the PCBX process.

4.9.1.2.2 Processing--The mobile processing unit is designed to process about 1.9 m^3 per hour of transformer oils containing up to 1000 ppm of PCBs. Processing equipment which could affect operating variables include: positive displacement pumps, automatically controlled heaters, reagent injection devices, PCB injection devices (for pure PCB destruction), mixing chambers, reaction vessels, heat exchangers, filter beds, and a vacuum degasser.

Reaction temperature must be regulated closely because any flow-through heaters or heat exchangers will directly affect the efficiency of the process. Proper mixing is also critical. The transformer oil and the reagent must be thoroughly mixed before entering the reaction vessel. Residence time in the reactor is critical to the process. Heat must be removed from the product effluent after leaving the reactor. Heat exchange between the oil that will enter the vacuum degasser and the product effluent must be carried out to cool the products to room temperature. The product stream will again need to be heated before entering the vacuum degasser. After vacuum degassing, the decontaminated oil can be returned to the transformer or kept in a retention tank.

The above processing steps should be evaluated according to how each will effect the overall process efficiency. Important process variables include the following:

- Reaction temperature: the temperature should be well below the flash point of the transformer fluid.
- Reaction times: the reaction times should be short for this process. Holding times of only a few minutes have been reported.
- Stoichiometry: Theoretical limitations exist for the minimum amount of reagent for any chemical reaction. To meet process objectives, the proper reagent amounts should be determined.

An assessment of optimum process conditions will need to be made. Lack of data prohibits the assessment at this time.

4.9.1.2.3 Pollution control--The overall pollution control equipment necessary for this process appears to be minimal. The overall process depends on the use of a reagent that strips the chlorine atoms from the biphenyl nucleus and generates naturally occurring chlorine compounds along with polymeric biphenyl residues. Control of the naturally occurring chlorine compounds can be accomplished using conventional methods. The polymeric biphenyl compounds could be stored for possible reuse. Conventional methods also exist for controlling these types of polymeric materials. The reagent used in the PBCX process is not public knowledge at this time. An overall evaluation of the necessary types of pollution control equipment must be done once detailed process information becomes available. The possibility of other toxic compounds being formed such as HCl or halogenated aromatic compounds will enter into the formal evaluation of the overall pollution control scheme. The generalized process description appears to indicate that selective filtrations and conventional oil treatment should be able to remove trace quantities of contaminants such as acids and toxic metals that could cause environmental damage. A pollution control evaluation should include how these contaminants will be disposed of.

4.9.1.2.4 Destruction efficiency--The original goal in process development was to remove all PCBs from the treated fluids. Experimental fluids used for laboratory studies have contained as little as 100 ppm and as high as 10,000 ppm PCBs. These fluids after treatment have contained 0 ppm and 40 ppm respectively, after reaction under optimum process conditions. The destruction efficiency for PCBs may be of the order of 99.6% more concentrated fluids.

4.9.1.3 Process Controls--

Possible process equipment which would need to be controlled are: positive displacement pumps, heaters, injection devices for reagents and PCB oils, the mixing chamber, heat exchangers, filters and the vacuum degassers.

Temperature and pressure must also be controlled in the reactor. Pressure and flow regulators must be used to control pressures and flow rates of all incoming and outgoing streams. Metering and mixing the reagent into the reactor must be controlled precisely. Obtaining the right residence time in the reactor is also critical for achieving good reaction results. Pollution control equipment should also be controlled automatically to insure against malfunctions and possible waste discharge to the environment.

4.9.1.4 Effluent Monitoring--

Because limited information exists about the composition of the effluent streams, it is difficult to speculate on the types of effluent monitoring needed in this process. The mobile processing unit should contain adequate effluent monitoring devices so the composition of each stream can be calculated. It is extremely important that the transformer oil and the reagent be well mixed before entering the reactor. This stream should be monitored to insure adequate mixing. All streams entering and leaving the vacuum degasser should be monitored to guard against the possibility of contaminated material being sent to storage or back to the transformer. Effluent monitoring must also be able to detect toxic compounds including PCBs, HCl, and other chlorinated hydrocarbons in all waste streams. At this time it appears that selective filtrations and conventional oil treatment should be able to remove trace quantities of acids and toxic metals. An overall assessment of effluent monitoring must include the pretreatment system as well as any auxiliary treatment processes. Adequate effluent monitoring equipment and strategy will depend directly on the nature of the effluent. Any solid waste effluents should be sampled by a grab technique. These streams should be analyzed carefully for PCBs and other toxic compounds. The plant should be equipped with automatic samplers on important effluent streams to insure that representative cross sections are removed.

4.9.1.5 Waste Characterization--

All samples were analyzed in the laboratory for total chlorine content. PCB solutions used in the laboratory studies contained Aroclors 1252 and 1254. Test solutions ranged from about 100 to 10,000 ppm PCBs.

4.9.1.5.1 Range of PCB concentration--The process appears to be highly successful in treating fluids containing as little as 100 ppm PCBs and as much as 10,000 ppm PCBs. As stated earlier complete destruction is claimed for fluids containing 100 ppm PCBs and greater than 99.6% destruction efficiency is claimed for fluids containing 10,000 ppm PCBs.

4.9.1.5.2 Limitations on constituents--Any contaminants such as acids, trace metals, and dissolved solids must be removed by pretreatment. Any substances that could cause corrosion or fouling of process equipment should also be eliminated. Moisture content of the oil should be very low, thus water must also be removed prior to treatment.

4.9.2 Environmental Factors

An environmental assessment study has not been developed for the PCBX process. The scale up study should include a preliminary environmental evaluation of the overall disposal operation as well as a detailed analysis of all possible reaction products. Each generic effluent stream should be analyzed for composition, and percent solids.

4.9.2.1 Potential Impacts of Disposal Operation--

Overall, the potential environmental impact of this disposal operation appears to be very low. Either very little or no toxic products will be produced. It is not known at this time whether there is a possibility of

PCB release to ambient air. If such a release does occur, it would likely be small. Analysis of all generic effluent streams should be an integral part of the overall disposal operation evaluation. Since the transformer oil is stripped of its PCB content and the chlorines are converted into natural occurring chloride substances, environmental damage should be minimal. The process unit appears to be equipped with special filtering devices as well as conventional reclamation equipment to remove the excess reagent and reaction products. In turn, the reclaimed and decontaminated insulating fluid may be sent back to the transformer for direct reuse. These two operations will lower the risk of environmental damage appreciably.

4.9.2.2 Impacts of Disposal or Process Wastes--

All the products generated by the PCBX process appear to be environmentally safe. The chemical reactions involved in the process convert chlorine contained in the PCBs to naturally occurring chlorides. The benzene nuclei are converted to polymeric solids which are insoluble in water, oil, and all other common solvents. It has been shown in laboratory studies that there is only one chlorine atom contained in a total of 38 to 62 benzene rings in these solids. It was further determined that the biphenyl polymer is 99% free of chlorine atoms. As stated above, the chloride products produced are claimed to be naturally occurring and non-toxic. The polymeric solids could be reclaimed for use as polymers, and the transformer oil is either stored for future reuse or sent directly back to the transformer. Based on the limited information available at this time, the environmental impact from process waste disposal appears to be minimal.

4.9.2.3 Potential Impacts of Accidents--

Spills or releases of PCBs from the PCBX process would appear to be the most likely sources of accidents. The PCBX process units should be evaluated as to how well accidental spills or releases could be prevented or contained. The possibility of toxic materials being discharged must be evaluated pursuant to EPA regulations. Construction of each mobile unit must be in accordance with EPA standards for hazardous waste disposal facilities. PCB storage and containment facilities should be evaluated with respect to PCB Regulations (40 CFR 761.42). If adequate facilities are not available it is recommended that the facility not be approved. A spill or release of PCBs from a PCBX processing unit could pose the following threats:

- Contamination of surface or groundwater
- Contamination of land areas where humans, animals, or croplands are exposed
- Contamination of areas that could lead to significant airborne movement of PCBs

Accidents caused by possible malfunctions of processing equipment could also occur. An assessment of these types of accidents should be carried out. Operator safety should be considered when evaluating process equipment efficiency. A detailed accident impact report should be developed for the PCBX process before implementation of the scaled up mobile unit.

4.9.3 Economic Factors

A cost analysis of Sunohio's PCBX process is not available at this time. It appears that a major capital investment is not required since the whole system is completely portable. According to Sunohio, the overall economics look favorable. Transformer oil can be decontaminated for $0.26-$0.77 per liter. The theoretical reagent cost is $1.1 per kg.

Cost credit may be earned by reusing the decontaminated heat transfer oil instead of discarding it.

4.9.4 Energy Factors

The amount of energy required per unit weight of PCB destroyed should be determined for this process. The energy requirement does not appear to be excessive at this time, although lack of data prohibits a quantitative analysis. An efficient series of heat exchangers used to heat and cool the treated oil should be able to reduce overall energy consumption appreciably. Some of the heat content of the PCB waste should be able to be recovered to produce steam. This will reduce the cost of energy by providing an energy credit.

4.10 WET AIR OXIDATION

4.10.1 Technical Factors

The catalyzed wet air oxidation process developed by IT Enviroscience, Inc. uses unique catalyst systems to accomplish a high level of PCB destruction at lower temperatures and pressures than conventional uncatalyzed wet oxidation processes. Because this technology is new, evaluation of the various technical factors involved is very difficult. Detailed evaluation should be carried out once scale up is completed.

4.10.1.1 State of Technology--

This technology is new and not completely developed. IT Enviroscience has recently completed feasibility testing and process development studies for the destruction of PCBs. Data from these studies are not available at this time, thus only a speculative assay of the technological impact can be undertaken now. Engineering development of the process will be required to define optimum operating conditions. A pilot plant is currently being constructed for development of a continuous process for destruction of PCBs. Scale up of a batch laboratory process for destruction of PCBs is also planned. Over 300 runs have been made in the IT Enviroscience laboratory-scale titanium stirred reactor to examine the destruction properties of a wide variety of hazardous wastes.

4.10.1.2 System Design--

IT Enviroscience system design objectives for the catalyzed wet oxidation of PCBs included the following:

- To achieve total destruction of PCBs and to minimize by products requiring disposal
- To reduce the amount of energy required for PCB disposal
- To have low reagent consumption
- To have few unit operations
- To create a low volume of effluents so that total containment and pollution control processes will be simplified
- To make the transition from laboratory to pilot plant fairly simple
- To be able to transport the process to facilities where the PCB waste problem exists

Only a general description of this process is available at this time, so that the treatment of system design parameters can only be taken as assumptions.

4.10.1.2.1 Pretreatment and feed--The ITE process has so far been applied to organic liquid residues and certain sludges and solid residues. Substances such as metals or dissolved solids should be eliminated by pretreatment. Substances that could cause corrosion or fouling in process equipment should also be eliminated prior to the reaction. Conventional pretreatment methods as well as any other suitable technique should be used for treating the possibly contaminated PCB fluid. Elimination of contaminants before processing is an effective way of lowering possible emissions and will make the process more efficient. The maximum PCB fluid input rate should be determined accurately. Because this input rate is critical, the feed system should be evaluated carefully. There may have to be an automatic flow cutoff that will be activated if the desired feed rate is exceeded or if other important process variables go out of tolerance. Overall, the pretreatment and feed system should be evaluated according to what types of materials will be handled or treated.

4.10.1.2.2 Processing--Optimum operating conditions will need to be determined for the scaled up version of this process. Under continuous feed conditions, the PCBs must be added to the reactor at this steady state destruction rate. When the catalyst solution needs to be disposed of, the reactor will need to be batch operated. It is important to note that PCB concentrations are reduced to ppm or ppb levels at this time. This switchover from continuous to batch operation should be analyzed closely in a pilot plant study. Heat and pressure are not used to drive the dissolution of oxygen from air in the process. Instead, the catalyst is used to promote the oxygen transfer. Operating conditions must be able to be adjusted to control the transfer of oxygen to the dissolved state by using gas and liquid phase reactions accompanying the catalyst reaction with the PCB material in the reactor. The overall conversion process should be evaluated around the unique features of these catalyst systems. The most important features in the processing step are that the nonvolatile organic material remains in the reactor until destroyed and that there is no aqueous bottoms product.

If batch processing of PCBs is to occur, the reactor must be sealed and heated. The reaction will proceed for 2 hours at 573°K and 7 MPa. The reactor must be cooled and vented. It is important to note that no vent gas is produced while the PCBs are being destroyed. The HCl produced by the oxidation must be distilled out of the reactor. The overall processing steps should be evaluated on the basis of overall destruction efficiencies achieved and the methods used to contain toxic or harmful effluents from each unit process.

4.10.1.2.3 Pollution control--The IT Enviroscience catalyzed wet air oxidation process utilizes an efficient system for controlling waste products. The only substances that leave the reactor are CO_2, N_2, water vapor, volatile organics, and any inorganic solids formed. Water and condensible organics are returned to the reactor. Any inorganic salts or acids formed can be removed by treatment in a closed loop stream of catalyst solution. Vent gases are low in volume and could be treated by conventional technologies, such as absorption, adsorption, or scrubbing. Because the nonvolatile organics remain in the reactor until destroyed and since there are no aqueous bottoms, pollution control should not pose any serious problems. Conventional pollution control technologies should be able to handle waste disposal problems readily. All generic effluent streams should be analyzed and monitored periodically for waste content. The overall pollution control system will need to be analyzed carefully upon scale up in accordance with EPA regulations.

4.10.1.2.4 Destruction efficiency--Over 50 runs were made on PCBs by ITE in a one liter titanium stirred reactor to define process conditions in the laboratory. Greater than 90% destruction of PCBs have been repeated, accomplished by oxidation at $523^{o}K$ for two hours. It is important to note that it is not necessary to achieve 99+% destruction of the PCB since the amount of PCBs that is not destroyed will remain in the reactor until it reacts and undergoes destruction.

4.10.1.3 Process Controls--

The following unit operations will need to be controlled either automatically or manually:

- Pretreatment and feed
- Addition and removal of reactants and products to the reactor
- The chemical reaction itself
- Treatment of product waste streams

An assessment of the types of controllers will need to be carried out.

Under continuous feed conditions, PCBs must be added to the reactor at their steady state destruction rate. Flow controllers will be needed to regulate this. Flow rates of all streams entering and leaving important process equipment should be controlled to insure smooth operation. Flow rates must also be controlled to achieve the optimum operating conditions.

Temperature control may also be critical to the system. Temperature will effect reaction rates and overall destruction efficiency. The process should contain adequate temperature monitoring and control devices located at appropriate stations throughout the system. The temperature in the reactor must remain within the defined operating range for high destruction efficiencies. Temperature must be controlled in any heat exchangers, condensers, columns and any other heat sensitive processing equipment.

Pressure control will be needed to insure against excessive pressure drops in heat exchangers, pumps, compressors, etc. Pressure may also need to be controlled in the reactor and any columns such as absorbers, scrubbers, etc.

All storage and processing tanks should be filled to appropriate levels to insure smooth and steady flow throughout the process. Level controllers should be installed in these tanks.

An overall assessment of the types of controllers needed to completely regulate this process should be done as part of the pilot plant study.

4.10.1.4 Effluent Monitoring--

As stated earlier, the substances that leave the reactor in the ITE catalyzed wet air oxidation process are CO_2, N_2, water vapor, volatile organics, and any inorganic solids formed. Condensible organics will be returned to the reactor. Effluent monitoring should center around the streams in which these components are contained.

Overall, the vent gases are low in volume but should be monitored, as they may contain various volatile organic substances. In evaluating the effluent monitoring system, the Regional Administrator should assess the capability of the facility operator to monitor all process effluent streams that could contain toxic levels of waste material. Ambient air samplers placed at specific locations around the reprocessing plant should be capable of detecting dilute concentrations of PCBs and other toxic compounds. Periodic air samples should be collected and analyzed for PCB content and total composition. In addition, post operational air samples should be collected and analyzed.

Liquid effluents should be monitored for flow rates, temperatures, pressures and composition. Each of these variables could critically affect overall process effectiveness. Each effluent stream could be monitored with conventional monitoring devices such as chromatographs and spectrometers. If a scrubber or absorption unit is used to remove chlorinated by products effluent streams from these units must be monitored and sampled on site. No limit on the PCB content of scrubber effluent streams is given except indirectly through reference to applicable effluent standards and any other state or Federal laws and regulations. The effluent monitoring capability of a facility should be determined by the facility operator's description of the appropriate streams.

Since various types of inorganic solid wastes may be generated, they should be sampled by a grab technique. Solids monitoring should be evaluated on the basis of amount and type of solid waste required and on the adequacy of the solid sampling locations.

4.10.1.5 Waste Characterization--

An accurate analysis of all effluent streams is needed to determine the nature of all process wastes. Only after these wastes are determined can effective disposal methods be applied. Scale up studies should include possible alternative procedures for handling the various process wastes.

4.10.1.5.1 Range of PCB concentration--The laboratory studies used five to six grams of Askarel (56% PCBs and 44% trichlorobenzene) to determine destruction efficiencies. This process may be adaptable over a wide range of PCB concentration. Transformer oils with >500 ppm PCBs might possibly be disposed of in this process.

4.10.1.5.2 Limitations on constituents--Any inorganic salts, acids, trace metals, and any substances that could cause fouling or corrosion of process equipment should be eliminated by pretreatment. Moisture should be eliminated before processing, and traditional oil cleaning methods should be used to eliminate trace impurities from the PCB oil. An extensive study should be carried out to determine the effect of the possible contaminants on the reaction and overall process variables. Any substance that can be oxidized or can react with the catalyst could interfere with the PCB oxidation. These substances should be determined and removed before processing the PCB oil.

4.10.2 Environmental Factors

It is extremely difficult to estimate environmental impacts of the ITE catalyzed wet air oxidation process at this time. Currently, data are not available so an environmental assessment will need to be done during a scale up study. The following impact analysis must be taken as speculative in nature.

4.10.2.1 Potential Impacts of Disposal Operation--

Minimal environmental impacts would be expected from the catalyzed wet air process operations during PCB disposal since the PCBs remain in the reactor until destroyed and there is no aqueous bottoms product. As stated earlier, CO_2, N_2, water vapor, volatile organics and inorganic solids leave the reactor. The water and condensable organics are returned to the reactor for further degradation. This step reduces the volume of toxic organic substances that could be contained in the effluent streams. The inorganic salts could easily be removed using conventional methods so environmental impact from them would be minimal. The vent gases are low in volume and could be treated by conventional techniques. Further research will need to be done to develop a detailed environmental assessment of this process.

4.10.2.2 Potential Impacts of Disposal of Process Wastes--

Analysis of all generic effluent streams will need to be carried out in order to evaluate the potential impacts of waste disposal.

Vent gases will be small in volume but may contain HCl and other toxic substances. Various types of chlorinated hydrocarbons could possibly be contained in the vent gases. Particulates could also escape with the vent gases. All of these substances can be safely removed by conventional methods so pose no real threat to the environment. If a scrubber or absorption column is used to remove contaminants, the effluent leaving the units must be monitored. No PCBs have been formed in the vent gas from the reactor, so possible environmental impact is minimal. The vent gas from the reactor and the vent gas from a scrubber are low and readily adaptable to polishing treatment for control of trace toxic compound releases.

4.10.2.3 Potential Impacts of Accidents--

PCB entry into the environment by vaporization into the atmosphere (and by subsequent deposition into land and water) and by spilling or dumping into water or onto land are the two major impacts of this process. The possibility of accidental release to the atmosphere from spills and leaks will continue to pose a threat as long as PCBs exist, but by using available control technology, it is possible to minimize PCB loss during transfer, storage, and disposal operations.

A spill or release of PCBs from a catalyzed wet air oxidation process facility could pose the following threats:

- Contamination of surface or groundwater
- Contamination of land areas where humans, animals, or croplands could be exposed
- Contamination of areas that could lead to significant airborne movement of PCBs.

Because of the limited amount of information available and because of the direct threat to the environment of potential PCB spills, the catalyzed wet air oxidation facility should be evaluated very carefully with respect to PCB storage and containment. An overall assessment of the potential impacts of accidents in all the units of the process will need to be carried out upon commercialization of this technology.

4.10.3 Economic Factors

Economic data for the IT Enviroscience catalyzed wet oxidation process for the destruction of PCBs are not available at this time. Information that should be evaluated include:

- Capital costs -- What will be the cost of the facility?
- Operating costs -- What will it cost to dispose of the PCB waste, per pound of waste, or per pound of PCB? What will be the cost of reagents, utilities, etc., and how do these costs vary with PCB content?
- Disposal costs -- What are the costs of disposing of wastewater and solid waste?
- Credits for products or by products -- Are soluble materials produced?
- Financial requirements -- What are the expected costs of closure and post closure monitoring and maintenance, and how will these costs be paid?
- Regulatory costs -- Will the regulatory process result in an increase in costs?

A cost analysis and feasibility study is currently being carried out by IT Enviroscience to determine the economic viability of this process.

Qualitatively this process seems to be economically feasible. Little or no added energy is required and no auxiliary fuel is consumed. Chemical consumption is small in this process, lowering the cost appreciably.

4.10.4 Energy Factors

IT Enviroscience cannot supply energy consumption data at this time. The amount of energy consumed per unit quantity of PCB waste should be compared to the similar figure for an Annex I incinerator. The energy utilization system should also be evaluated for possible energy credits such as the possibility of recovering any waste heat for use in steam generation or for the reclamation of materials which could be used as fuel.

According to IT Environscience, little or no added energy is required and no auxiliary fuel is consumed. The heat of reaction provides ample heat to drive the reaction of the catalyst, PCB liquid, and oxygen, Qualitatively, it appears that this process does not use an excessive amount of energy, although a thorough heat balance will need to be performed around each unit process to determine the overall heat demand.

5. EVALUATION OF BIOLOGICAL PROCESSES

As noted in Section 3.2, biological disposal methods are all based on the ability of microorganisms to degrade toxic organic compounds, such as PCBs. The major differences between the various methods lie in the means of supporting and contacting the microorganisms with the fluid containing the species to be degraded, means of providing oxygen (air or O_2) to the microorganisms, and in pre- and post-treatment steps.

The literature review indicated that most commercial aoplications of biological processes are to aqueous streams containing relatively small amounts of organic compounds. Laboratory studies have shown that pure Aroclor mixtures are degraded and that degradation rates are inversely related to increasing chlorine substitution. U.S. Air Force studies (U.S. Air Force, 1974) showed that some microorganisms degraded the very concentrated Herbicide Orange components over a period of years. Commercial land farming is used to degrade oil-contaminated industrial aqueous wastes. However, PCBs are more refractory than the major Herbicide Orange components and oils. No studies on purely non-aqueous PCB-containing materials were found.

5.1 ACTIVATED SLUDGE METHODS

5.1.1 Technical Factors

5.1.1.1 State of Technology--

Activated sludge methods are well developed and widely used at commercial scale for treatment of sewage and industrial wastewaters. As a well developed technology, most aspects of an activated sludge treatment facility need only be evaluated cursorily.

The literature search did not locate any work describing deliberate PCB disposal by activated sludge methods at the commercial scale. A laboratory scale study (Tucker, et al., 1975) showed percentage degradations of Aroclors fed at 1 mg/48 hr ranging from 81 percent for Aroclor 1221 to 15 percent for Aroclor 1254. Tri-, tetra-, and pentachloro isomers were undergraded. The finding of PCBs (mono-through decachloro isomers) in samples of municipal sewage sludge indicates that some plants cannot handle PCB degradation (Erickson and Pellizzari, 1979). No references to commercial or lab scale applications to non-aqueous streams were found.

It is concluded that activated sludge methods cannot be considered technically applicable at this time to general disposal of PCBs and PCB Items. While trace quantities of PCBs could be fed into a commercial scale process and while some degradation will occur, destruction will not be complete, and the amounts fed will be so small as not to appreciably aid the PCB disposal problem.

Further research is warranted, but the research might most profitably be pursued in the following areas: 1) more effective treatment of sewage and wastewater already contaminated by PCBs, 2) treatment of PCB-contaminated dredge spoil, and 3) developing microorganisms effective at degrading PCBs.

5.1.1.2 System Design--

In general, an activated sludge sewage/wastewater treatment facility consists of the following unit operations: 1) pretreatment and feed, 2) primary clarifier with or without recycle of excess activated sludge, 3) equalization basin, 4) aeration basin(s), 5) secondary clarifier(s), 6) dewatering, 7) drying, and 8) final disposal. Because applications of activated sludge treatment are well developed for sewage and wastewater, only those aspects of system design that affect PCB disposal need be considered. It should be noted again that activated sludge methods are biological processes and, hence, have limited ability to handle high concentrations of toxic compounds, such as PCBs.

5.1.1.2.1 Pretreatment and feed--Types of pretreatment that may be necessary include: 1) maintenance of an appropriate PCB input rate, 2) nutrient addition, 3) pH adjustment, 4) dilution, 5) extended acclimation, or 6) removal of toxic elements (e.g., precipitation of heavy metals).

Activated sludge treatment is a lengthy process. Thus, there must be foreknowledge of the adequacy of destruction efficiencies. Given this knowledge, the maximum PCB input rate can be predetermined. Because the PCB input rate is a critical value, the feed system will have to be evaluated carefully. There must be an automatic cutoff that will function if the desired feed rate is exceeded and if other important process variables go out of tolerance.

Nutrient addition for PCB disposal may or may not be necessary. Information supplied by the facility operator should identify whether nutrient addition is necessary. The same consideration applies to pH adjustment and removal of toxic elements.

Dilution may or may not be necessary. For example, if the source of PCBs to the treatment plant is PCB-contaminated dredge spoil, then dilution may be necessary to keep solids fed to the process basins about 20 percent Similarly, a concentrated PCB feed will need to be diluted or fed at a rate sufficiently slow in order to preclude toxic effects to the microorganisms.

Acclimation may be necessary to allow the microorganisms to adjust to PCBs being fed to the process. Thus, the initial PCB feed rate may have to be much lower than that ultimately achievable in order to build up a suitable population of microorganisms.

5.1.1.2.2 Processing--Unit processes of principal interest to PCB disposal and those requiring evaluation are primary clarification, equalization basins, and aeration basins. PCBs tend strongly to adsorb on inorganic particulate matter (e.g., soil particles). Thus, the clarification stage must be evaluated to determine whether all settled particulate material is eventually fed to the aerator basin(s). Because of the tendency of PCBs to adsorb on particles, the material from the clarifier should not be discarded without either being analyzed for PCBs or being processed through the aeration basin.

The equalization process should be evaluated with respect to PCB vapor emissions and the fate of any settled particles. Although the amount of PCBs fed into the system should be small, low molecular weight PCBs (e.g., monochloro isomers) may escape from solution. Also, any particles that settle in the equalization basin should, unless analyzed for PCBs, eventually be transferred to the aeration basin.

The aeration basin(s) is the heart of an activated sludge process, for it is where the microbial degradation actually occurs. Process design considerations for aeration basins include provision for adequate levels of dissolved oxygen in the waste water, maintenance of a proper concentration ratio of active biomass to organics, and sufficient mixing and contact time. Typical design parameters for aerobic digestion are (EPA, 1974):

- Solids retention: 15-20 days
- Dissolved oxygen: 1-2 mg/l
- Temperature: $> 288^{o}K$

Information supplied by the owner/operator of a facility proposing disposal of PCBs should include enough process information so that the Regional Administrator can compare the proposed process with other similar processes. Additionally, the information should clearly state any changes in process parameters necessary for PCB disposal.

After digestion is complete, the sludge is conditioned to facilitate dewatering and is then dewatered, dried, and disposed of.

5.1.1.2.3 Pollution control--Activated sludge wastewater treatment processes produce three generic effluent streams: dried sludge, supernatant water, and gas. The bulk of undestroyed PCBs would probably be found in the dried sludge because PCBs tend to adsorb strongly on particles and because the more highly chlorinated PCBs tend to be the isomers least degraded by microorganisms. PCBs adsorbed in the sludge should be relatively resistant to being leached. Dried sludge from such a treatment process should be carefully investigated for residual PCBs in order that the appropriate means of disposal can be used.

The supernatant liquid from an activated sludge treatment process should also be carefully analyzed despite the fact that the bulk of undegraded PCBs should be adsorbed in the sludge. Sampling and analysis is particularly necessary if the activated sludge process is the last stage (i.e., secondary treatment only) and the supernatant will be discharged directly into the environment (e.g., river, lake, sea).

Aerobic activated sludge wastewater treatment processes typically do not generate significant odors. Water and CO_2 are the primary products of microbial digestion of organic matter fed into the system. If the degradation process stops at monochlorobiphenyls, then traces of these may escape in the vapor phase. Research should indicate whether this may occur. If significant amounts of low molecular weight PCBs can escape as vapor, then there are several options:

- Seal those unit processes that can emit PCBs and treat the emitted gases (adsorbers, incinerator, or partial recycle through the digester)
- Reduce PCB feed rate so that emissions are acceptable

5.1.1.2.4 Destruction efficiency--In a pilot scale study, Tucker, et al. (1975) showed destruction efficiencies (percentage degradations) ranging from 81 percent for Aroclor 1221 to 15 percent for Aroclor 1254. Destruction efficiencies of current processes decrease rapidly with increasing chlorine substitution. It is doubtful whether any activated sludge process will be capable of destruction efficiencies equivalent to those of high efficiency boilers or Annex I incinerators.

5.1.1.3 Effluent Monitoring--

As noted above, biological treatment methods, such as activated sludge, are not likely to achieve high levels of destruction efficiency. Thus, if such a method is used for PCB disposal, careful effluent monitoring is necessary to determine the extent of degradation and assess the potential environmental impacts of undestroyed PCBs.

Conventional activated sludge wastewater treatment plants are usually well equipped with test ports for liquid and sludge sampling because extensive routine monitoring for water and sludge quality parameters is performed. In a "Trial Burn" situation, daily composite water and sludge samples should be taken in order to determine the rate of PCB degradation. Because aerobic activated sludge treatment plants are typically not enclosed, gaseous emissions of PCBs probably would best be sampled by means of high volume ambient air samplers modified with polyurethane foam as an adsorbent (Stratton, et al., 1978). Several such samplers should be used with at least one upwind of the source of PCB emissions.

5.1.1.4 Waste Characterization--

5.1.1.4.1 Form of waste--Activated sludge treatment processes seem best suited to handle aqueous streams or dredge spoil contaminated with PCBs. If PCB Items are to be treated, they should be finely shredded.

5.1.1.4.2 Range of concentrations--As noted earlier, biological processes are not well suited to high concentrations of toxic organic compounds. With extended acclimation, higher levels of such compounds may be tolerated. No information on tolerable levels of PCBs was found. Given that EPA's fresh water criterion for PCBs of 1.5 ppb is intended to provide adequate protection for freshwater life (EPA, 1978), it seems unlikely that PCB concentrations more about 3-4 orders of magnitude greater would be tolerated.

5.1.1.4.3 Limitations on constituents--PCB wastes containing excessive concentrations of toxic heavy metals will require pretreatment prior to entering the aeration basins. The extent and type of treatment will depend on the process and experience of the owner/operator.

5.1.2 Environmental Factors

Because no references on disposal of PCBs by activated sludge treatment were found, it is difficult to estimate environmental impacts of such a disposal operation.

5.1.2.1 Potential Impacts of Disposal Operation--

Minimal environmental impacts would be expected from activated sludge process operations during PCB disposal because of the expected small amounts of PCBs involved and because such processes routinely operate without adverse impact. There is a possibility of PCB release to ambient air, but releases should be small. Testing, however, is needed.

5.1.2.2 Potential Impacts of Disposal of Process Wastes--

As discussed earlier, activated sludge treatment processes generate three types of generic effluent streams: sludge, supernatant water, and vapors. The bulk of residual PCBs would be expected in the sludge. The PCB content of the sludge will be affected by several later process steps: drying (multiple hearth, flash dryers, tray dryers, spray dryers) and final reduction to reduce volatile organics (incineration, wet air oxidation, pyrolysis). Final disposal methods for solids from activated sludge processes include cropland application, land reclamation, power generation (co-fired with other fuels), sanitary landfill, and ocean dumping (EPA, 1974).

The method of final sludge disposal is an important consideration because it determines the form of the sludge residue and liquid unit processes to be employed. The method of final sludge disposal is also an important consideration in selecting a plant for PCB disposal. If the drying and final reduction stages of sludge treatment leave PCB residues, then certain final disposal options, such as cropland application, land reclamation, or ocean dumping, may pose undesirable environmental impacts.

The supernatant water, after completion of the activated sludge treatment, is not expected to contain appreciable amounts of PCBs although additional research is necessary. However, subsequent use of the supernatant water is an important consideration. Activated sludge treatment is a secondary treatment, and the supernatant water is not of drinking water quality. Tertiary treatment of the supernatant water can upgrade it to drinking water standards. Generally, however, supernatant water from activated sludge treatment is dumped into rivers, lakes, or oceans. Unless testing determines that the PCB content of supernatant water is at or below applicable standards, then direct discharge of the supernatant could cause undesirable environmental impacts. It would probably be undesirable with respect to public concern to discharge the supernatant water into a tertiary treatment stage if the treated water is used directly for drinking water.

5.1.2.3 Potential Impacts of Accidents--

A spill or release of PCBs from an activated sludge treatment facility may pose the following threats:

- Contamination of surface or groundwater
- Contamination of land areas where humans, animals, or croplands could be exposed
- Contamination of areas that could lead to significant airborne movement of PCBs

A spill into the process itself poses potentially more significant threats and is cause for very careful control of PCBs fed into the process. These threats are:

- Creation of a large volume of contaminated water and sludge
- Contamination of surface or groundwater if supernatant water is directly discharged into the environment

- Contamination of surface water or drinking water if the supernatant is discharged into a tertiary treatment section

As noted in Section 2.1, regulations pursuant to the Clean Water Act currently require, and to RCRA will require, facilities disposing of PCBs to prepare spill prevention, control, and countermeasures plans. These plans are intended to detail safe handling procedures of hazardous materials (i.e., PCBs), but they also must address prevention and control procedures when a release of PCBs occurs. The goals are to prevent discharges and to minimize impacts of spills. An adequate SPCC plan should minimize the potential for spills and, hence, potential environmental impacts from spills.

An activated sludge treatment plant is not typically in the hazardous waste disposal business. Thus, it is not expected that such a plant will be constructed in accordance with RCRA standards for hazardous waste disposal facilities. Because of the very direct threat to the environment of potential PCB spills, an activated sludge treatment facility should be evaluated very carefully, especially with respect to PCB storage and containment. If adequate storage (mandated by the PCB Regulations, 40 CFR 761.42) and adequate containment facilities are not available, it is recommended that the facility not be approved.

5.1.3 Economic Factors

The most expensive unit processes in a typical activated sludge wastewater treatment facility are the sedimentation basin, sludge dewatering, and chemical storage/feed facilities. The major operating and maintenance costs would be for labor and chemicals. Tables 7 and 8 summarize important capital and operating and maintenance costs for a 0.31 m^3/sec activated sludge wastewater treatment facility located in Chicago, Illinois. The cost estimates are based on mid-1978 dollar values.

It appears that an activated sludge treatment facility processing PCBs should have costs similar to those presented in Tables 7 and 8, although a detailed economic analysis would need to be done because of possible regulatory and disposal cost requirements. Both capital and operating costs appear to be moderate.

TABLE 7. SUMMARY OF CAPITAL COSTS FOR ACTIVATED SLUDGE
(Hansen et al, 1978)

Capital Cost Category Module	Costs†						
	Site Preparation	Structures	Mechanical Equipment	Electrical Equipment	Land	Total	Other Land (ft^2)
Sedimentation Basin	$ 29,700	$ 241,000	$ 766,000	$ 2,020	$ 25,500	---	34,300
Aerated basin	10,500	116,000	171,000	---	12,800	---	17,200
Clarifier	995	115,000	22,300	172	645	---	867
Sludge dewatering	178	42,600	919,000	9,190	4,120	---	5,530
Chemical feed	14,710	213,000	935,000	---	6,220	---	8,362
Chemical feed	8,330	107,000	29,500	---	1,520	---	2,039
Chemical pump	---	---	1,530	---	---	---	---
Chemical pump	---	---	1,470	---	---	---	---
Waste pump	---	---	10,800	---	---	---	---
Waste pump	---	---	10,800	---	---	---	---
Sludge pump	---	---	4,490	---	---	---	---
Yard piping	900	---	55,200	---	---	---	---
Total	65,313	834,600	2,927,090	11,382	50,805	---	68,298
Supplemental capital costs	---	141,303#	---	---	---	---	---
Subtotal of capital costs	---	---	---	---	---	4,030,493	---
Working capital**	---	---	---	---	---	97,021	---
AFDC ‡	---	---	---	---	---	201,525	---
Grand total of capital costs	---	---	---	---	---	4,329,039	---

* Scale = 5,000 gpm; total nitrogen = 2.0 ppm; total phosphorus = 1.0 ppm, BOD = 150

† Mid-1978 dollars

Building

** At one month of direct operating costs
‡ Allowance for funds during construction at 5% of capital costs

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TABLE 8. SUMMARY OF FIRST YEAR OPERATING AND MAINTENANCE COSTS FOR ACTIVATED SLUDGE
(Hansen et al, 1978)

		Labor		Costs ‡				
O&M Cost Category Module	Type 1 Operator 1 ($7.77/hr)	Type 2 Operator 2 ($9.19/hr)	Type 3 Laborer ($6.76/hr)	Energy Electrical ($0.035/KWH)	Maintenance Costs	Chemical Costs	Total	Other KWH (yr)
Sedimentation basin	$3,911	$ 276	$ 40,850	$ 102	$ 68,600	$ ----	---	2,914
Aerated basin	3,521	831	33,686	3,790	34,100	----	---	103,286
Clarifier	10,636	755	111,078	102	2,230	----	---	2,914
Sludge dewatering	2,933	900	30,637	70,500	9,240	2,020	---	2,014,285
Chemical feed	--	--	---	---	900	699,000	---	---
Chemical feed	--	--	---	---	800	8,740	---	---
Chemical pump	--	--	---	35	---	----	---	1,000
Chemical pump	--	--	---	17	---	----	---	486
Waste pump	--	--	---	8,630	---	----	---	246,571
Waste pump	--	--	---	8,630	---	----	---	246,571
Sludge pump	--	--	---	4,490	---	----	---	128,286
Yard piping	--	--	179	---	363	----	---	---
Total	21,001	2,762	216,430	96,296	116,233	709,760	---	2,751,313
Supplemental O&M costs	--	--	---	---	1,770	----	---	---
Subtotal of direct O&M costs	--	--	---	---	---	----	$ 1,164,252	---
Administrative overhead#	--	--	---	---	---	----	232,850	---
Debt service and amortization **	--	--	---	---	---	----	704,531	---
Real estate taxes and insurance †	--	--	---	---	---	----	86,581	---
Total first year operating costs	--	--	---	---	---	----	2,188,214	----

* Scale = 5,000 gpm

‡ Mid-1978 dollars

# At 20% of direct operating costs

** At 10% interest over 10 years

† At 2% of total capital

5.1.4 Energy Factors

Generally, energy consumption is low for activated sludge wastewater treatment facilities. The amount of energy required per unit of PCB waste processed would need to be determined in the overall economic analysis.

5.2 TRICKLING FILTER METHODS

5.2.1 Technical Factors

5.2.1.1 State of Technology--

Trickling filter methods are well developed and widely used for degradation of dilute, non-biocidal, organic waste streams.

A literature search did not uncover any work describing PCB disposal by trickling filter methods. Likewise, no references to commercial scale applications to non-aqueous streams were found. It is concluded that trickling filter methods cannot be considered technically feasible for the disposal of PCBs and PCB items at this time.

5.2.1.2 System Design--

Basically, a trickling filter wastewater treatment facility is designed to distribute a uniform amount of wastewater over the trickling filter media by a flow distributor. A large amount of the wastewater applied to the filter should pass through rapidly, and the remainder should slowly trickle over the surface of the slime. BOD removal occurs by biosorption and coagulation from the rapidly moving portion of the flow and by progressive removal of soluble constituents from the more slowly moving portion of the flow.

System design should be based on the following: 1) amount of available food to control the quantity of biological slime produced, 2) hydraulic dosage rate, 3) type of media, 4) type of organic matter, 5) amount of essential nutrients present, 6) nature of the type of biological growth.

5.2.1.2.1 Pretreatment and feed--Types of pretreatment that may be necessary include: 1) maintenance of an appropriate PCB feed rate, 2) nutrient addition, 3) removal of toxic elements such as heavy metals and toxic compounds, 4) dilution, and 5) pH.

Since the PCB input rate is critical to the process, the feed system will need to be evaluated critically. Automatic shutoff devices should be installed that would be activated if the optimum PCB feed rate is exceeded or if other important process variables deviate from their specified ranges.

Nutrient addition, pH adjustments and removal of toxic elements may need to be carried out depending on the nature of the waste. Information supplied by the facility operator should be adequate to determine if the above operations need to be carried out.

Dilution may be necessary if the PCB waste fed into the facility is too concentrated to be filtered effectively. Since the quantity of biological slime produced is controlled by the available food, dilution may be needed to adjust the PCB feed stream to acceptable levels.

5.2.1.2.2 Processing--The following factors could affect the performance of this process if adapted to handle aqueous streams containing PCBs: 1) wastewater characteristics, 2) trickling filter media, 3) trickling filter depth, 4) recirculation, 5) hydraulic and organic loading, 6) ventilation, and 7) temperature of applied wastewater.

The strength of wastewaters can vary greatly over a daily period. An effective way of minimizing these variations is to recirculate filter effluent through the primary clarifier.

Various types of trickling filter media should be compared on the basis of physical properties. Specific surface area and percent void space will have a pronounced effect on PCB processing. Greater surface areas permit a larger mass of biological slime per unit volume, while increased void space allows for enhanced oxygen transfer and higher hydraulic loadings.

Trickling filter depth will directly affect the treatment efficiency of the process and is a major design parameter. The treatment efficiency of a synthetic media trickling filter is much more responsive to variations in depth than a stone media trickling filter.

Recirculation of the effluent can be used to improve the efficiency and operation of stone media trickling filters.

Hydraulic loading rates directly affect the performance of a trickling filter. Hydraulic loading will closely predict the performance of a stone media trickling filter.

Proper ventilation of trickling filters is necessary to maintain aerobic conditions throughout the filter media. It should be determined whether or not forced ventilation is necessary.

The efficiency of trickling filters is affected by temperature changes. The effect of temperature on filter performance may show up when comparing summer efficiencies with winter efficiencies.

Information supplied by the owner/operator of a facility proposing disposal of PCBs should supply enough process information so that the Regional Administrator can compare the proposed process with other similar processes. The information should clearly state any changes in process parameters necessary for PCB disposal.

5.2.1.2.3 Pollution control--Trickling filter wastewater treatment produces two generic effluent streams: dried sludge and final waste effluent. Most of the undestroyed PCBs would probably be found in the dried sludge since PCBs tend to adsorb strongly on particles and because highly chlorinated PCBs tend to be poorly degraded by microoganisms. The PCBs adsorbed in the sludge should be relatively resistant to being leached. The dried sludge should be carefully analyzed for residual PCBs, so that an appropriate disposal method can be chosen.

The final waste effluent should also be carefully analyzed even though most of the undegraded PCBs should be adsorbed in the sludge. Sampling and analysis will be needed if the effluent is discharged directly into the environment (e.g., rivers, lakes, seas, etc.).

Trickling filter wastewater treatment processes typically do not generate significant wastes. Water and CO_2 are the main products of microbial digestion of organic matter fed into the system. Research will be necessary to determine the amount of chlorinated biphenyls that may pass through the filter and into the secondary clarifier. Conventional pollution control devices should be adequate to prevent excessive PCB release from the system.

5.2.1.2.4 Destruction efficiency--As stated earlier, an extensive literature search could not uncover any trickling filter processes applied to PCB destruction. It can be expected that destruction efficiencies will decrease with increasing chlorine substitution. At this time it appears doubtful whether any activated sludge process will be capable of destruction efficiencies equivalent to those of high efficiency boilers or Annex I incinerators.

5.2.1.3 Effluent Monitoring--

As stated above, trickling filter treatment methods are not likely to achieve high levels of destruction efficiency. If such a process is used for PCB disposal, careful effluent monitoring will be needed to determine the extent of PCB degradation and to assess the potential environmental impacts of undestroyed PCBs.

Conventional trickling filter wastewater facilities are normally well equipped with efficient effluent monitoring devices because extensive monitoring for water and sludge quality is necessary. Daily composite water and sludge samples should be taken in order to determine PCB degradation rates.

5.2.1.4 Waste Characterization--

5.2.1.4.1 Form of waste--Trickling filter treatment processes are best suited to handle aqueous streams contaminated with PCBs. If solids are to be treated, they should be finely shredded.

5.2.1.4.2 Range of PCB concentration--As stated earlier, trickling filter processes are not well suited to high concentrations of toxic organic compounds. No information on possible tolerable levels of PCBs could be found. Given that EPA's fresh water criterion for PCBs of 1.5 ppb is intended to provide adequate protection for fresh water life (EPA, 1978), it seems unlikely that PCB concentrations of more than 3-4 orders of magnitude greater could be tolerated.

5.2.1.4.3 Limitations on constituents--PCB wastes containing excessive concentrations of toxic materials such as heavy metals will require pretreatment prior to entering the trickling filter. The type of pretreatment will depend on the nature of the toxic substances.

5.2.2 Environmental Factors

Because no references on disposal of PCBs by trickling filter treatment were found, it is extremely difficult to estimate the environmental impacts of this disposal process.

5.2.2.1 Potential Impacts of Disposal Operation--

Minimal environmental impacts would be expected from trickling filter process operations during PCB disposal because the quantity of PCBs being processed would be small. There could be slight releases of PCBs to ambient air so air sampling and testing is needed.

5.2.2.2 Potential Impacts of Disposal of Process Wastes--

As stated earlier, trickling filter treatment processes generate two types of generic effluent streams: dried sludge and final effluent water. Most of the residual PCBs would be expected to be found in the sludge. The PCB content of the sludge could be affected by subsequent processing steps such as drying. Final disposal methods for solids from trickling filter processes include: land reclamation, cropland application, sanitary landfill, and ocean dumping (EPA, 1974).

Final sludge disposal methods must be chosen carefully since they will determine possible environmental impacts. If the final drying and reduction stages of the sludge treatment leave PCB residues, then certain final disposal options such as cropland application or land reclamation may be undesirable.

The final effluent water should not contain any appreciable amounts of PCBs. Trickling filter treatment is a secondary treatment, and the effluent water is not of drinking quality. Tertiary treatment should be able to upgrade the effluent water to drinking quality. However, effluent water from trickling filter treatment is usually dumped into rivers, lakes, or oceans. Testing should be done to insure that the PCB content of the effluent water meets applicable standards.

5.2.2.3 Potential Impacts of Accidents--

A spill or leak of PCBs from a trickling filter treatment facility could pose the following threats:

- Contamination of surface groundwater
- Contamination of land areas where humans, animals, or croplands could be exposed
- Contamination of areas that could lead to significant airborne movement of PCBs

As noted in section 2.1 regulations pursuant to the Clean Water Act currently require, and to RCRA will require, facilities disposing of PCBs to prepare spill prevention and control plans. These plans should address prevention and control procedures when a release of PCBs occurs.

Since a trickling filter treatment facility does not specialize in hazardous waste disposal, it is not anticipated that this type of plant would be constructed in accordance with RCRA standards for hazardous waste disposal facilities.

A trickling filter treatment facility should be evaluated very carefully with respect to PCB storage and containment. Adequate storage (mandated by the PCB Regulations, 40 CFR 761.42) must be available in order for the treatment facility to be approved.

5.2.3 Economic Factors

Capital costs for a trickling filter facility will depend heavily on the following unit processes:

- Filtering
- Operation of the sedimentation basin
- Sludge dewatering
- Feed pretreatment

The major operating and maintenance costs will be for chemicals and labor. Tables 9 and 10 depict capital and operating costs based on mid-1978 values for a 0.31 m^3/sec trickling filter wastewater facility located in Chicago, Illinois.

At this time, it can only be concluded that the costs should be similar if the process is adapted to handle aqueous streams contaminated with dilute amounts of PCBs. Other costs, such as regulatory and special disposal costs may need to be figured into an economic evaluation if the process is adapted to PCB disposal. Overall, it appears that moderate capital and

TABLE 9. SUMMARY OF CAPITAL COSTS FOR TRICKLING FILTER PROCESS
(From Hansen et al, 1978)

Capital Cost Category Module	Costs†						Quantities	
	Site Preparation	Structures	Mechanical Equipment	Electrical Equipment	Land	Total	Land (ft²)	Other Volume (gal)
Trickling filter	$ 69,400	$723,000	$ 85,020	$ ---	$ 93,300	----	---	2,300,000
Sedimentation basin	29,700	241,000	766,000	2,020	25,500	----	34,300	----
Clarifier	995	115,000	22,300	172	645	----	867	----
Sludge dewatering	143	34,100	735,000	7,350	3,290	----	4,430	----
Chemical feed	14,710	213,000	935,000	---	6,220	----	8,362	----
Chemical feed	8,330	107,000	29,500	---	1,520	----	2,039	----
Chemical pump	---	---	1,530	---	-----	----	---	----
Chemical pump	---	---	1,470	---	-----	----	---	----
Sludge pump	---	---	4,490	---	-----	----	---	----
Yard piping	1,125	---	72,500	---	-----	----	---	----
Total	124,403	1,433,100	2,652,810	9,542	130,475	----	49,998	2,300,000
Supplemental capital costs	---	141,303#	---	---	-----	----	---	----
Subtotal of capital costs	---	---	---	---	-----	$ 6,791,633	---	----
Working capital**	---	---	---	---	-----	60,325	---	----
AFDC‡	---	---	---	---	-----	339,582	---	----
Grand total of capital costs	---	---	---	---	-----	7,191,540	---	----

* Scale = 5,000 gpm; TSS = 500 ppm; percent solids (wt/wt) = 20

† Mid-1978 dollars

# Building

** At one month of direct operating costs

‡ Allowance for funds during construction at 5% of capital costs

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TABLE 10. SUMMARY OF FIRST YEAR OPERATING AND MAINTENANCE COSTS FOR TRICKLING FILTER PROCESS
(From Hansen et al, 1978)

	Costs†							
	Labor							
O&M Cost Category Module	Type 1 Operator 1 ($7.77/hr)	Type 2 Operator 2 ($9.19/hr)	Type 3 Laborer ($6.76/hr)	Energy Electrical ($0.035/KWH)	Maintenance Costs	Chemical Costs	Total	Other KWH (yr)
Trickling filter	$ 1,172	$ 208	$ 19,384	$ ---	$ 9,029	$ ---	---	---
Sedimentation basin	3,911	276	40,850	102	68,600	---	---	2,914
Clarifier	10,636	755	111,078	3,102	2,230	---	---	2,914
Sludge dewatering	2,933	900	30,637	56,400	7,390	1,610	---	1,611,428
Chemical feed	---	---	---	---	900	349,000	---	---
Chemical feed	---	---	---	---	800	1,750	---	---
Chemical pump	---	---	---	35	---	---	---	1,000
Chemical pump	---	---	---	17	---	---	---	486
Sludge pump	---	---	---	863	---	---	---	24,657
Yard piping	---	---	204	---	363	---	---	---
Total	18,652	2,139	202,153	60,519	89,312	352,360	---	1,643,399
Supplemental O&M costs	---	---	---	---	1,770	---	---	---
Subtotal of direct O&M costss	---	---	---	---	---	---	$ 725,136	---
Administrative overhead#	---	---	---	---	---	---	145,027	---
Debt service and amortization **	---	---	---	---	---	---	945,499	---
Real estate taxes and insurance ‡	---	---	---	---	---	---	143,831	---
Total first year operating costs	---	---	---	---	---	---	1,959,492	---

* Scale 5,000 gpm

† Mid-1978 dollars

# At 20% of direct operating costs

** At 10% interest over 15 years

‡ At 2% of total capital

operating costs would be realized.

5.2.4 Energy Factors

Typically, energy consumption is low for trickling filter wastewater treatment facilities. The amount of energy required per unit of PCB waste processed would need to be determined in the overall economic analysis.

5.3 SPECIAL BACTERIAL METHODS

An intensive literature search could not uncover any information about the usage of any of the special bacterial methods for PCB disposal. Lack of information means little can be said about important technical factors at this time. Many of the same technical and environmental problems that apply to activated sludge and trickling filter processes will also apply to these other bacterial methods, so that reference should be made to Sections 5.1 to 5.2.

Because there are insufficient data to indicate the effectiveness of any of the newer biological disposal methods, further testing is warranted. Mutant bacterial inoculum in combination with existing treatment systems, such as activated sludge or trickling filter processes, should be researched as a viable PCB disposal method.

It is recommended that research be carried out in the following technical and environmental areas: 1) quantification and assessment of PCB losses to the environment because of vapor pressure or volatility problems, 2) research to implement the use of the most favorable of the bacterial methods for PCB disposal, 3) pilot plant construction to attempt the biodegradation of PCBs contained in a non-aqueous medium, 4) integrated biological disposal systems should be developed to utilize the best properties of each different system, 5) residual toxicity tests should be performed for each process, and 6) a complete economic feasibility study should be performed for each system.

6. COMPARISON OF THERMAL AND NON-THERMAL METHODS

As stated earlier, EPA considers non-thermal destruction processes the "alternative methods" to incineration of PCBs. The basis for evaluation of an alternative non-thermal system for PCB destruction is its performance relative to a thermal system. As is stated in the PCB Regulations, 40 CFR 761.10(e), an alternative system must be demonstrated to "achieve a level of performance equivalent to Annex I incinerators or high efficiency boilers". This section will compare several non-thermal methods with the thermal (Annex I incinerators and high efficiency boilers) processes as a basis for providing guidance on implementing the possible non-thermal methods. The technical, environmental, economic, and energy factors discussed in Sections 4 and 5 will provide the basis for this comparison.

As noted in a study by Ackerman et al. (1981), essentially complete destruction of PCBs can be achieved in both Annex I incinerators and high efficiency boilers. Generally, incineration of PCB fluids and PCB materials with concentrations greater than 500 ppm in an Annex I incinerator is extremely efficient. The same holds true for high efficiency boilers in which PCB liquids in the 50-500 ppm range may be burned.

None of the alternative methods described in this report are at commercial scale, so that only limited data are available. There are, therefore, substantial technical, environmental, economic, and energy information gaps. Some of the methods have not been applied to PCB degradation but offer interesting possibilities. Other methods have only been applied to PCBs in dilute aqueous solution but are covered because of potential adaptability to PCBs in dilute organic solution (e.g., mineral oil dielectric fluid). Comparison of these alternative methods with thermal methods is necessary, but many of the comparisons are qualitative in nature.

Destruction efficiencies, for those methods that have been so tested, are well below the performance requirements of Annex I incinerators or high efficiency boilers. Currently, none of the alternative methods meet the destruction efficiency requirements of the PCB Regulations although there are other factors that must be considered in evaluating alternative methods.

Table 11 compares major characteristics of the thermal (Annex I incineration and high efficiency boiler) PCB destruction processes and the nonthermal methods.

In general, activated carbon adsorption processes have been primarily used for the removal of organic materials from dilute wastewater, i.e., solutions in which the concentrations of the compounds to be removed are 0.1 percent by weight. Since the lower cutoff limit for PCBs is 50 ppm, it is not expected that activated carbon adsorption processes could compete against either Annex I incineration or high efficiency boilers.

With only modest research, activated carbon adsorption methods could be applied to PCB disposal. However, only liquid PCBs could be treated. Ultimate disposal of PCB-contaminated charcoal would be by incineration, volatilization of adsorbed PCBs, recycling the cleaned carbon, and incineration of the PCB vapors. Based on these considerations, it does not seem likely that activated carbon adsorption is cost competitive. However, recovery of uncontaminated mineral oil may be an offsetting factor.

As stated in Section 4.2, catalytic dehydrochlorination of PCBs has been successful in the laboratory only. System design parameters and processing variables are not well defined at this time. Feed pretreatment, reactor design, and pollution control will need to be quantified before any meaningful conclusions can be made.

A direct comparison between a chlorinolysis plant able to handle PCBs with either Annex I incineration or high efficiency boilers may only be speculated on at this point. Important system design factors such as reactor design and process and pollution control schemes will need to be developed. Incineration of waste residues may be needed. This could decrease the usefulness of this process for PCB disposal. The destruction efficiency of PCBs in existing chlorinolysis units would be very low since polychlorinated aromatic compounds are not converted to any appreciable extent.

The Goodyear process may be adaptable to the conversion of PCBs to nontoxic products and is capable of being performed on-site in existing equipment. However, the overall conversion of PCBs is only 92 percent which is

TABLE 11. TECHNICAL, ENVIRONMENTAL, AND ECONOMIC COMPARISON OF THERMAL AND NON-THERMAL PCB DESTRUCTION/CONVERSION METHODS

Destruction or Conversion Method	Potential for Large Scale Application	Current Status of Technology as Applied to PCB Processing	Destruction Efficiency	Feedstock	PCB Range (ppm)	Overall Environmental Impact	Overall Economic Impact
Annex I Incineration	High	1	>99.99%	g,l,s	>50	4,5	9
High efficiency boilers	High	1	>99.99%	l	<50	4,5	9
Activated Carbon Adsorption Processes	High	3	Not applicable	a	Dilute amounts	4,5,11	7,10
Catalytic Dehydrochlorination	Medium	2	99+%	l,g	>50	5,12	7,10
Chlorinolysis	Low	3	Low	l	Not Applicable	4,5	9,10,15
Goodyear Process	High	3	92%	l	<500	4	6,10
Microwave Plasma	Medium	2	95%	l,g	50-500	4,5	7
Ozonation Processes	Medium	3	Not applicable	a	Dilute amounts	5,12	9
Photolytic Processes	Low	2	90-95%	l	>50	5,12	7
Sodium-Oxygen-Polyethylene Glycol	Medium	2	95%	l	50-500 and >500	12	7,10,15
Sunohio Process	High	3	99+%	l	50-500 and >500	4	6,10,15
Catalyzed Wet Air Oxidation	Medium	2	99+%	a,l,s	50-500 and >500	3	7
Activated Sludge	Low	3	Not applicable	a	Dilute amounts	12	7
Trickling Filter	Low	3	Not applicable	a	Dilute amounts	12	7
Special Bacterial Methods	Low	3	Not applicable	a	Dilute amounts	12	7

1	Method is currently used commercially	11	Requires recycling or disposal of adsorption medium
2	Proven research method only	12	Potential residual toxicity of by products
3	Limited or no data base	13	Not applied to PCBs
4	Potential controllable method with minimum environmental impact	14	Potential release of chlorocarbons to the environment
5	Potential solid residue or wastewater disposal problem	15	Potential return on investment
6	Low capital investment and moderate operating costs	s	Solid
7	Moderate capital investment and operating costs	a	Aqueous
8	Large capital investment and moderate operating costs	g	Gas
9	Large capital investment and operating costs	l	Liquid
10	Resource recovery option		

far below the 99.9%+ destruction efficiencies found for Annex I incinerators and high efficiency boilers. This lower destruction efficiency will detract from possible advantages, such as product recovery.

PCB destruction by microwave plasma is underdeveloped at this time, thus direct comparisons to the thermal PCB destruction processes are difficult to make. Laboratory destruction efficiencies are lower than those for Annex I incinerators or high efficiency boilers. Process and pollution control schemes may be very complex because of the elaborate circuitry and corrosive nature of the waste effluents. These schemes may require excess capital expenditure making the overall process impractical.

UV-ozonolysis has been applied to destruction of PCBs contained in wastewater only. It is doubtful that this process could be applied effectively to non-aqueous systems. This process can only handle PCBs in the ppb range, thus direct quantitative comparisons with either Annex I incineration or high efficiency boiler destruction would be meaningless. Although UV-ozonolysis offers some interesting possibilities for PCB removal from dilute aqueous streams at fairly low cost and environmental impact, it cannot be considered as a reasonable alternative to thermal destruction at this time.

Photolytic PCB destruction methods are not well developed. Quantitative comparisons with thermal destruction methods cannot be made at this time. As stated earlier, intensive research will need to be carried out to determine final products and residues resulting from PCB reactions with various wavelengths of light. Although a 90-95 percent yield of dechlorinated PCB was found in the experiments performed by Ruzo, et al. (1974), inadequate data exist to draw any meaningful conclusions regarding commercialization of photolytic processes at this time.

The use of molten sodium metal dispersed in polyethylene glycols to degrade PCBs has barely been researched in the laboratory. Lack of technical data prohibits any meaningful speculation on the utility of this process for large scale PCB disposal. Laboratory destruction efficiencies (∿95%) are below those found for both thermal processes. Elaborate pollution control schemes and safety procedures may be needed because of the evolution of large amounts of hydrogen gas. This could make the process too complex and expensive to be practical. Optimization studies will need to be carried out before any meaningful conclusions can be drawn.

Technical information gaps and lack of process data prohibit an effective comparison to be made between the Sunohio PCBX process and the thermal methods. Destruction efficiencies are not as high, and the method has not been proven to be reliable on an industrial scale. Product recovery and reuse as well as mobile unit on-site processing are convenient advantages of the PCBX process, but may not outweigh the overall lower destruction efficiency.

The IT Enviroscience catalyzed wet air oxidation process has been researched in the laboratory but has not been applied commercially. Destruction efficiencies have been found to be between 91-99+%, depending on PCB concentration, but commercialization is needed to determine large scale applicability. Destruction efficiencies have not been determined concisely, thus prohibiting quantitative assessment at this time. Unless a consistent destruction efficiency >99.99% is achieved it is unlikely that this process could compete with either Annex I or high efficiency boiler PCB destruction methods.

The biological processes described in Section 3 have been used primarily for the removal of organic and inorganic materials from dilute wastewater where PCB concentrations will be in the ppb range. It is not expected that any of these methods could compete against either Annex I incineration or high efficiency boilers. Environmentally, each biological process may require an excessive number of checks or safeguards because of the possibility of PCB release to the environment. The possibility of PCB spills and groundwater contamination appear to be more likely for each biological process than for either of the thermal destruction methods. An intensive literature search could not uncover any studies that were aimed at applying these biological processes to PCB detoxification, of non-aqueous material.

Generally, it is not expected that any existing biological treatment facilities will be constructed in accordance with RCRA standards for hazardous waste disposal.

7. APPROVAL PROCESS FOR ALTERNATIVE PCB DISPOSAL METHODS

Chapter 7 provides a suggested process for approval of alternative PCB disposal methods because:

- It is anticipated that most alternate methods will have to undergo testing in lieu of a Trial Burn regardless of whether the material to be disposed of is mineral oil dielectric fluid from PCB-contaminated transformers of PCB concentration >50 ppm and ≯500 ppm (notification only is necessary for disposal in high efficiency boilers), is other PCB-contaminated liquids of PCB concentrations >50 ppm and ≯500 ppm (approval necessary for disposal in high efficiency boilers), or is any PCB liquid or Item of PCB concentration >500 ppm (approval is necessary and disposal can be by Annex I incinerator only).
- The approval process for alternate methods described in the PCB Regulations is not as systematized as it is for Annex I incinerators and high efficiency boilers.

The suggested approval process presented in Chapter 7 is not technically detailed because of the large number of processes described in this interim guideline document and because none of the processes are fully defined and at the commercial scale. Reference should be made to process descriptions presented in Chapter 3 and to process evaluations presented in Chapters 4 (Physicochemical Methods) and 5 (Biological Methods).

7.1 INTRODUCTION

The PCB Regulations provide (see also Section 2.1) at Section 761.10(a) that a person who is required incinerate any PCBs or PCB Items, who can demonstrate that an alternative destruction method exists, and who can demonstrate that the method can achieve a level of performance equivalent to Annex I incinerator or high efficiency boilers may submit a written request to the cognizant Regional Administrator for an exemption from the Annex I incineration requirements. The applicant must show that the method will not present an unreasonable risk of injury to health or the environment.

On the basis of information in the waiver application and any other available information, the Regional Administrator may, at his discretion, approve the use of the alternate method if he finds that the "method provides PCB destruction equivalent to disposal in an Annex I incinerator and will not present an unreasonable risk of injury to health or the environment" (761.10(e)).

Section 761.10(c)(5)(iii) provides for alternatives to Annex I incineration or Annex II chemical waste landfills for disposal of dredged materials and municipal sewage treatment sludges that contain PCBs. The written application must, based on technical, environmental, and economic considerations indicate that disposal in an incinerator or chemical waste landfill is not reasonable and appropriate and that the alternative method will provide adequate protection to health and the environment. The Regional Administrator may request other information that he or she believes to be necessary for evaluation of the alternate disposal method.

In summary, the owner/operator of an alternative disposal method must submit to the cognizant Regional Administrator either a request for a waiver or an application containing required information. The Regional Administrator is responsible for evaluating the information, determining the need for additional information, determining appropriate conditions and provisions for an approval, and issuing (or not issuing) an approval.

It is recommended that any alternative PCB disposal method be evaluated according to the formal procedures described for Annex I incinerators (40 CFR 761.40) which are shown schematically in Figure 15. Appropriate points for public participation are noted on Figure 15.

7.2 EVALUATION OF EXEMPTION REQUEST AND INITIAL REPORT

Section 761.10(e) provides that any person who is required under Subpart B to incinerate PCBs or PCB Items may apply for an exemption if he can demonstrate that:

- An alternative method exists
- The method can provide a level of performance equivalent to that of Annex I incinerators or high efficiency boilers
- The method will not present an unreasonable risk of injury to health or the environment

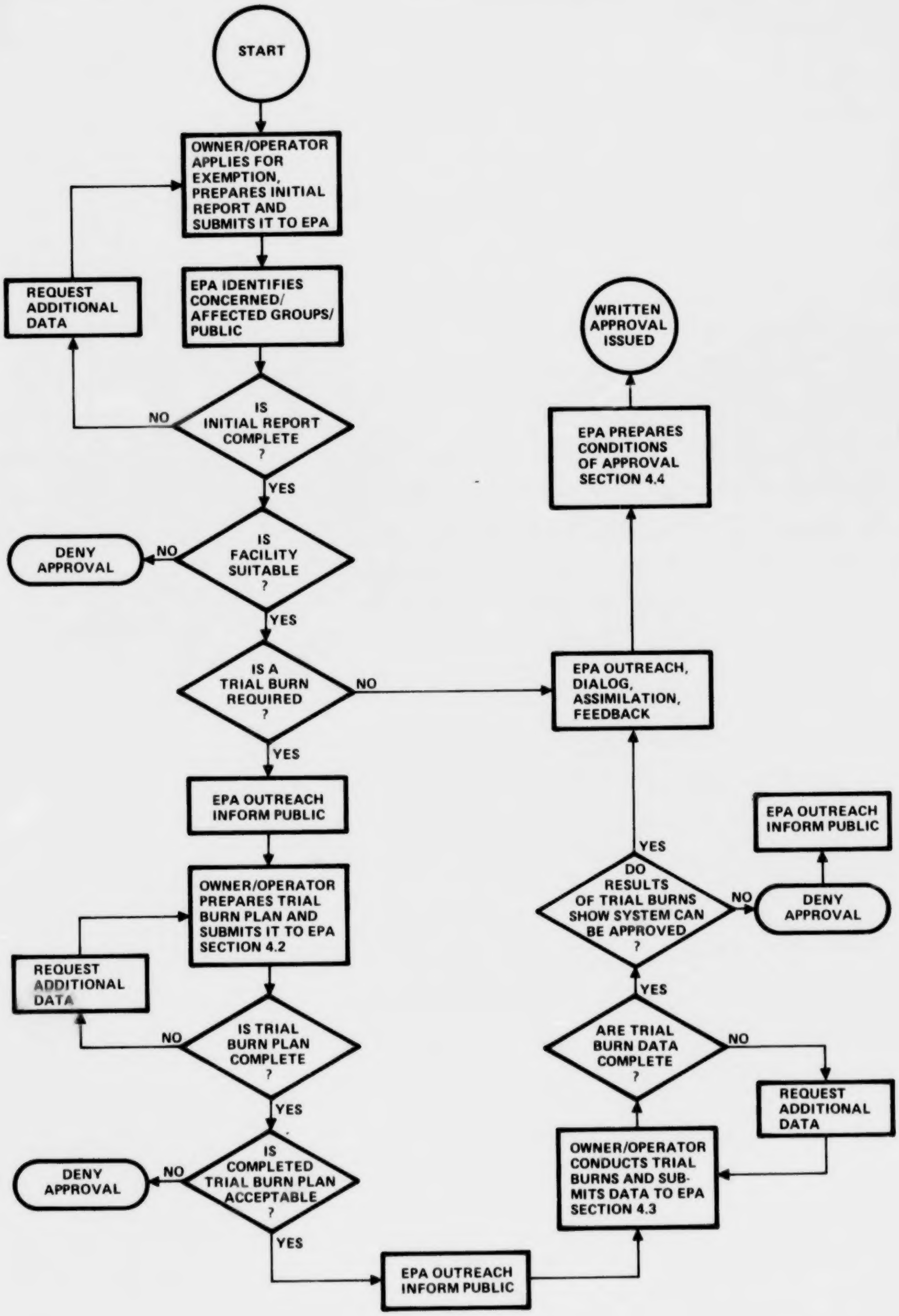
START
OWNER/OPERATOR APPLIES FOR EXEMPTION, PREPARES INITIAL REPORT AND SUBMITS IT TO EPA
REQUEST ADDITIONAL DATA
EPA IDENTIFIES CONCERNED/ AFFECTED GROUPS/ PUBLIC
NO
IS INITIAL REPORT COMPLETE ?
YES
DENY APPROVAL
NO
IS FACILITY SUITABLE ?
YES
IS A TRIAL BURN REQUIRED ?
NO
YES
EPA OUTREACH INFORM PUBLIC
OWNER/OPERATOR PREPARES TRIAL BURN PLAN AND SUBMITS IT TO EPA SECTION 4.2
REQUEST ADDITIONAL DATA
NO
IS TRIAL BURN PLAN COMPLETE ?
YES
DENY APPROVAL
NO
IS COMPLETED TRIAL BURN PLAN ACCEPTABLE ?
YES
EPA OUTREACH INFORM PUBLIC
WRITTEN APPROVAL ISSUED
EPA PREPARES CONDITIONS OF APPROVAL SECTION 4.4
EPA OUTREACH, DIALOG, ASSIMILATION, FEEDBACK
EPA OUTREACH INFORM PUBLIC
YES
DO RESULTS OF TRIAL BURNS SHOW SYSTEM CAN BE APPROVED ?
NO
DENY APPROVAL
YES
ARE TRIAL BURN DATA COMPLETE ?
NO
REQUEST ADDITIONAL DATA
OWNER/OPERATOR CONDUCTS TRIAL BURNS AND SUBMITS DATA TO EPA SECTION 4.3

Figure 15. Flow chart for approval process for non-thermal methods.

Types of information that will permit the Regional Administrator to evaluate the information supplied include:

- Location of the process and the owner/operator
- Detailed description of the process, including general site plans and design drawings of the process
- Engineering reports or other information on the anticipated performance of the process, including any testing of destruction capability
- Sampling, monitoring, and analysis equipment and facilities available
- Waste volumes and PCB contents expected to be processed
- Any Federal, state, and local permits or approvals granted
- Plans and schedules for complying with the approval requirements of the PCB Regulations
- Chemical and physical properties of the waste(s) to be processed
- Emission control system(s) and operating data
- Process control system operation
- Waste storage facilities

The Regional Administrator has the responsibility to evaluate the exemption request in light of the information supplied to determine the need for additional information, to determine the appropriate conditions and provisions for an approval, and to issue or deny an approval. On the basis of the information supplied and any supplemental information requested, the Regional Administrator may require a test in lieu of a Trial Burn.

7.3 EVALUATION OF A TRIAL BURN PLAN

This section presents a brief discussion of and guidelines for evaluation of testing in lieu of a Trial Burn.

The PCB Regulations do not specify the amount of testing to be performed. On the basis of Best Engineering Judgement and past practice of Trial Burns, it is recommended that the following test strategy be employed:

- One background test while operating the process under typical conditions with a waste as similar as possible to the PCB containing waste. Collect all pertinent gas, liquid, and solid samples and analyze for PCBs and organochlorines (RCLs).

- Three tests while processing PCB wastes under operating conditions similar to those of the background test. Collect all pertinent gas, liquid, and solid samples and analyze for PCBs and RCLs.

7.3.1 Operational Data

The Trial Burn plan should be evaluated with respect to the adequacy of descriptions of process control monitoring plans and instrumentation. Critical assessments should be made of fail-safe instrumentation for shutting off PCB feed in the event of process failures. Critical process parameters requiring monitoring are described in Chapters 4 and 5 for each of the processes discussed in this report.

7.3.2 Monitoring, Sampling, and Analysis

The Trial Burn plan should be evaluated with respect to the adequacy of descriptions of monitoring, sampling, and analysis methodologies (Appendix B), instrumentation, and capabilities. Test port locations should be assessed for the capability of permitting the test personnel to withdraw sufficient and representative samples.

7.4 EVALUATION OF TRIAL BURN DATA

The object of a test in lieu of a Trial Burn of a non-thermal method is to determine whether it meets the destruction efficiency performance requirements of Annex I incinerators or high efficiency boilers, as appropriate. This section briefly describes methodology for evaluating data resulting from such testing.

Once Testing is completed, data should be reviewed for completeness. That is, a review of all test data should be made to determine whether all required data have been taken. This review should be completed before the test team leaves the site. Table 12 is a brief list of generic kinds of data appropriate to testing the non-thermal method described in the report.

Once the test team has returned to the laboratory and once analysis have been completed, data reduction is performed. After data reduction, a review should be made to assess the validity and representativeness of the data and results. This review involves the following steps:

- Engineering assessment - Determine any periods of anomalous operation, such as start up, shut down, or off-normal operations. Remove data taken during these periods. These data might be used to characterize transient effects but should not be used to characterize normal operations.

TABLE 12. TYPES OF DATA FROM TESTS IN LIEU OF A TRIAL BURN

I. Feed Rates
   - Liquid PCBs, in
   - PCB Items, in
   - PCB content of PCB Items
   - Reagents, in
   - Gas, out
   - Liquid, out
   - Solids, out

II. Analytical Results, PCB content of:
   - Liquids in: PCBs, RCLs
   - Solids in: PCBs, RCLs
   - Reagents in: PCBs, RCLs
   - Liquids out: PCBs, RCLs
   - Solids out: PCBs, RCLs

III. Gas Analysis (if appropriate)
   - HCl content
   - PCB content
   - RCL content
   - Particulate matter

- Statistical testing - After removal of data from anomalous operating periods, statistical testing for outliers should be performed. The Dixon Outlier Test (Dixon and Massen, 1969) is recommended.
- Data quality assessment - Calibration data for test, analysis, and process instrumentation should be examined for acceptability in terms of recency and accuracy. Review of other quality control checks should be made to assess validity of the test results.

Data satisfying the above assessment methodology can then be used to characterize the test in lieu of a Trial Burn. A recent EPA manual (EPA, 1980) of sampling and analysis methods for complying with RCRA testing requirements recommends the use of confidence limits.

The confidence limit is used to characterize the mean of a set of data. The confidence interval is

$$u = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

where u = true population mean

$\bar{x}$ = mean of test results

s = standard deviation about the mean

t = "Student's t" at 95% confidence and (n-1) degrees of freedom

n = number of values comprising the mean

The confidence interval provides a range of values within which the true mean of the sampled population should be within the specified degree of confidence (95% confidence is recommended) upon repeated testing under the same test conditions.

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APPENDIX A

RECOMMENDED TEST METHODS

A.1 RECOMMENDED METHOD FOR SAMPLING STACKS OR DUCTS

EPA (1978) published an interim sampling and analysis manual for PCB disposal. If an alternate PCB disposal method produces a gaseous emission stream that could contain PCBs, then it is recommended that the EPA (1978) method described in Attachment E be employed. This recommended sampling train is a modified EPA Method 5 train (EPA, 1976) and consists of a heated probe, heated particulate filter, two water filled impingers, an empty impinger, an adsorbent tube filled with Florisil, a NaOH filled impinger, a silica gel filled impinger, a vacuum pump and a dry gas meter. A detailed operating procedure is given in (EPA, 1978). This train has been used in six recent PCB Trial Burns (EPRI, 1980; Moore, et al., 1980; Rollins, 1980; Tennessee Eastman, 1979; and Zelenski and Haupt, 1979).

This train is operated isokinetically and traversed across stack diameters according to Method 5 procedures, as detailed in EPA, 1978.

It is recommended that a Method 5 train modified with a water cooled XAD-2 ^{R} resin trap be used for sampling organochlorine compound emissions from stacks and ducts of non-thermal PCB disposal processes. XAD-2, a porous polymer resin, has been extensively chracterized for retention of organic compounds (Adams, et al., 1977; Gallant, et al., 1978; and Piecewicz, et al., 1979). XAD-2 has two advantages over Florisil: 1) more extensive characterization for trapping organic compounds than Florisil and 2) greater capacity than Florisil. A disadvantage is that XAD-2 is more difficult to clean (i.e., remove background organic compounds).

Additional characterization of PCB trapping and recovery efficiency on Florisil should be performed. The work of Haile and Baladi (1977) showed that the recovery of a dichlorobiphenyl isomer was only 47% under the following conditions: 1) 4-hour sampling period, 2) ambient temperature, 3) 20 lpm (0.7 cfm) sampling rate, and 4) 150 mm long x 22 mm diameter trap containing 7.5 g of Florisil. These conditions are essentially those required by Attachment E of EPA's Interim Manual (EPA, 1978) and used in the six Trial Burns cited above. It is widely recognized that combustion and environmental ageing (e.g., weathering, photolysis) dechlorinate more highly chlorinated PCBs to ones with lower degrees of chlorination. Thus, the recommended sampling system employing Florisil lacks adequate trapping efficiency for those chlorobiphenyl isomers (mono- and dichlorobiphenyls) that ought to be enhanced by non-thermal destruction methods.

A.2 RECOMMENDED METHOD FOR SAMPLING AMBIENT AIR

The method developed by Stratton, et al., (1978) for sampling for PCBs in ambient air is recommended. This system is based on a standard high volume sampler modified to incorporate a plug of polyurethane foam after the filter.

Stratton, et al.,(1978) started with the system developed by Bidelman and Olney (1974) as a starting point and modified it to improve its performance. The authors describe the modifications made, the laboratory tests performed to verify the method, and field testing. They also describe the extensive polyurethane foam cleanup procedure necessary before it can be used for sampling.

Validation studies performed by Stratton, et al. (1978) indicated that each PCB isomer has a different retention time in polyurethane foam. Retention times are generally in order of decreasing volatility. Thus, monochlorobiphenyl is the least retained PCB species. They found maximum sampling period to be about 2 hours at 0.7 m^3/min (84 m^3 or 3000 ft^3). The authors' conclusions were:

- Collection and recovery efficiencies are independent of flow rate in the range of 0.6 to 1.0 m^3/min (21-28 cfm).
- Ambient temperature and humidity have no effect on collection efficiency.
- Breakthrough or loss of PCB isomers occurs in the order monochlorobiphenyl, dichlorobiphenyl, and higher substituted species.
- Quantitative collection (85%) is assured when the sampling period does not exceed 2 hours.
- The mean collection efficiency for all tests conducted with Aroclors 1016 and 1242 was 101 ± 10%.

The authors conducted several field tests of the system. Urban ambient air in Jacksonville, FL, was sampled. Several samples of 2 to 24 hours duration were taken over a 24 hour period. Values ranged from 15 ng/m^3 to

25 ng/m^3 at one location and from 3 ng/m^3 to 36 ng/m^3 at a second location. The second location was sampled again with a 6-hour sampling period. No PCBs were detected. A third test at the second location was performed with 4-hour sampling durations over a 24-hour period. PCB concentrations varied from 4 ng/m^3 to 9 ng/m^3. Several other field tests are also described.

A.3 RECOMMENDED METHODS FOR SAMPLING LIQUIDS

Liquids are typically taken by what is termed grab sampling. A contained liquid is generally taken by tap sampling. A tap, either existing or installed in a line or container, is opened, and the sample is conducted into an appropriate container. (Samples for organic analyses are best taken in amber glass bottles with non-adhesive Teflon lid liners.) If the liquid is at elevated temperature, it is passed through a cooling coil before entering the sample container. Dipper sampling is appropriate to sampling sluices, ponds, open discharge streams, and rivers.

A grab sample is representative of the liquid stream only at the time of acquisition. Consequently, samples need to be taken repeatedly throughout the duration of a test in order that process variations that give rise to composition changes in the stream are adequately tested. If numerous samples are necessary, an automatic composite sampler, such as that described by Grant (1978), can be used.

Additional methods of sampling liquids are provided in a recent EPA manual (EPA, 1980) published in support of physical/chemical testing required by RCRA.

A.4 RECOMMENDED METHODS FOR SAMPLING SOLIDS

Solids are usually sampled by grab techniques using scoops, shovels, thiefs, triers, and augers, depending on the nature of the solid materials lump size, density, consistency, etc. Scoops and shovels are used to sample granular or powdered material in bins, shallow containers, and conveyor belts. A thief sampler is used to sample dry ganules or powders, the particle size of which is less than one-third the diameter of the thief. The thief sampler consists of two slotted concentric tubes usually made of stainless steel or brass. The outer tube has a conical pointed tip which is used to penetrate the material being sampled. The inner tube is rotated to open the sampler (admit sample) and close the sampler (isolate sample for withdrawal). A trier sampler is used to sample sticky solids or soil. It consists of a tube cut in half lengthwise for most of the length. The open end is pointed and sharpened for penetration. An auger is used to sample hard or packed materials and soils. It is made of sharpened spiral blades attached to a central metal shaft. The spiral blades make for a "screw like" action as the auger is turned.

When sampling solids, consideration must be given to obtaining a representative sample. Generally, a solid process effluent stream should be sampled repetitively during a test to ensure obtaining a representative sample.

The American Society for Testing Materials has published a procedure for preparing composite samples of solids (ASTM, 1978). EPA (1980) has published a manual which covers sampling of solids.

A.5 RECOMMENDED ANALYSIS METHODOLOGY

PCBs have been detected by numerous researchers in all environmental media. Indeed, these compounds are considered to be ubiquitous. Significant levels of contamination have been detected in air, waters, aquatic sediments, soils, and various biota. There are only limited data on PCB emissions from combustion sources and incinerators.

There are several factors which complicate the assessment and interpretation of PCB emissions. First, the term PCB applies not to a single chemical species but to a class of compounds, related by chemical structure and degree of chlorine substitution on the parent molecule, biphenyl. There are 209 possible isomers, ranging from 3 monochloro isomers to 1 decachlorobiphenyl isomer. PCBs are seldom manufactured or used as pure isomers. In industrial applications, PCBs are made and marketed as mixtures, and each of these mixtures contains significant fractions of many of the possible isomers. For example, Aroclor 1242, a commercial PCB product, is comprised of 54 identified isomers (Hutzinger, et al., 1974). Sissons and Welti (1971) identified 69 isomers in Aroclor 1254. Such mixtures have been detected in numerous environmental media. The fact that a class of compounds and not a single identifiable chemical species is to be detected and measured greatly increases the complexity of a chemical analysis.

The second complicating factor is that degradation processes change the relative amounts of isomers in the mixture(s) being disposed of. Thus, process stream samples will tend to be enriched in the higher volatility, lower molecular weight PCBs and deficient in the lower volatility, higher molecular weight PCBs. Thus, interpretation of analytical results can be difficult.

A third complicating factor is interferences. Many of the non-thermal processes will emit a substantial number of compounds, many of which exhibit extraction and analytical behavior similar to PCBs. Environmental samples frequently contain a variety of pesticides which also exhibit analytical behavior similar to that of PCBs.

A.5.1 General Analytical Methodologies

Gas chromatography (GC) is by far the most widely used analytical method of separating compounds in the vapor phase, and thus GC provides qualitative information about a sample.

Various detectors are employed in GC analysis to measure compounds after separation. The most widely used detector is the electron capture detector (ECD). The ECD responds, in principle, to electronegative atoms, such as halogens. The ECD is enormously sensitive and is capable of detecting picogram quantities of halogenated compounds such as PCBs. The ECD has a limited dynamic range, and its response is linear over only several orders of magnitude. A major complication in the use of the ECD is that response factors to various compounds vary over several orders of magnitude, depend strongly on the degree of halogenation, and depend to a lesser extent on halogen substitution pattern in isomers with the same degree of halogenation. Thus, the analyst's experience and proper preparation of analytical standards are very important in the analysis of PCBs using the electron capture detector.

A less sensitive, and thus less widely used, detector is the flame ionization detector (FID). The FID responds, in principle to carbon-hydrogen bonds. In fully halogenated compounds, there are no carbon-hydrogen bonds; and the FID has negligible response. The FID is capable of detecting nanogram and sub-nanogram quantities of partially halogenated compounds, such as PCBs.

The most powerful current technique for organic compound analysis is gas chromatography followed by mass spectrometry (GC/MS). In theory, every compound will produce a unique mass spectrum. Thus, compounds are separated in the GC, and they are identified and quantified by the mass spectrometer. In practice, it is difficult or impossible to distinguish the mass spectra of similar positional isomers. In general, however, GC/MS provides sufficient identification power for PCB analysis. GC/MS analysis is generally much less sensitive and considerably more expensive than GC/ECD analysis although there are techniques for enhancing the sensivity of GC/MS. Thus, GC/MS is frequently used to confirm the presence of PCBs in a sample after GC/ECD analysis.

A.5.2 Quantitation

Three general methods of quantifying PCBs have been used either individually or in combination (EPRI, 1980). These methods are described below.

A.5.2.1 Pattern Recognition--

The most common method of quantifying PCBs in environmental samples involves comparing the multipeak gas chromatographic elution pattern generated by the sample (after cleanup procedures to remove pesticides and other potentially interfering compounds) with the elution patterns of commercial PCB mixtures. (Because one company was the principal manufacturer of commercial PCBs, each mixture is quite reproducible with respect to isomeric composition and concentration.) This comparison is relatively subjective. The decision is then made as to what commercial product most closely matches the sample pattern. The quantity of PCB present in the sample is calculated by comparing areas of one or more major peaks in the sample with matching peaks in the commercial mixture of known concentration. It is assumed explicitly that all PCB isomers are present in the sample in the same proportion as in the commercial mixture chosen for quantitation. This assumption is generally incorrect. Quantitation by pattern recognition was described in detail by Hutzinger, et al. (1974).

Pattern recognition has the following advantages:

- It is well suited to gas chromatographic analysis, which is simpler and less expensive than GC/MS analysis.
- It identifies a commercial mixture which can aid in identifying the source of the contamination.
- It is more sensitive than some GC/MS methods and allows for more accurate quantitation if samples are not complex or altered by combustion, weathering, or biological processes.

Pattern recognition has the following disadvantages:

- Combustion source and environmental samples will have altered patterns because of depletion of some isomers. Thus, recognition of a pattern may not be possible. Even if a pattern is recognizable, quantitation of a PCB mixture with an altered isomeric or concentration composition would be inaccurate and potentially misleading.
- Many environmental samples also contain various pesticides, some of which have extraction and chromatographic behavior similar to PCBs. Thus, pattern recognition may not be possible, and quantitation may be inaccurate.

A.5.2.2 Derivatization--

Derivatization involves converting all PCB isomers in a sample to decachlorobiphenyl (DCB) by reaction with antimony pentachloride. DCB is fully chlorine substituted, so that there is only a single isomer.

Derivatization has the following advantages:

- It considerably simplifies the analysis by converting all PCB isomers to a single isomer.
- It considerably reduces the detection limit when an electron capture detector is used because ECD sensitivity increases with increasing halogen substitution (although not linearly).
- It enables the analyst unequivocally to quantitate DCB.
- It minimizes the necessary analytical judegements involved in the physical measurement of the chromatogram of a multicomponent mixture.

Derivatization has several disadvantages:

- As Armour (1972) stated, derivatization to DCB should only be used as a confirmatory technique because of the possible presence of interfering compounds.

- The result of the conversion to and quantification of DCB is generally reconverted to an amount of the Aroclor mixture in the original sample. Correction factors range from 0.38 for Aroclor 1221 to 0.79 for Aroclor 1262 (Armour, 1972). The actual factor cannot be known without accurate knowledge of the Aroclor originally present. Because of changes in isomer distribution and concentration in a sample from a disposal/destruction source, considerable error can be induced in conversion of a DCB value to the original Aroclor mixture.
- The method is subject to false positives. Haile (1976) found several extracts of samples taken at a coal-fired utility plant that produced DCB upon perchlorination in which PCBs could not be confirmed by GC/MS analysis of unperchlorinated portions of the sample. Haile concluded that the extracts contained biphenyl and/or related aromatic compounds that could be converted to DCB and that GC/MS was necessary for verification of PCBs. EPRI (1980) noted false positives in the Trial Burn at ENSCO.

A.5.2.3 Measurement of Individual Components--

Because of the disadvantages of pattern matching and derivatization, Webb and McCall (1973) proposed analysis by GC using ECD detection using Aroclor standards in which the quantitative composition of each peak is known. Using GC/MS and GC with an electrolytic conductivity detector, Webb and McCall determined the empirical formula and the amount of chlorine represented by each peak in a series of Aroclor standards.

Eichelberger, et al. (1974) proposed a GC/MS method in which selected ions were monitored. Their study indicated that single ions characteristic of mono- through hexachlorobiphenyl could be monitored and thus provide enhanced sensitivity over the usual method of scanning a large mass range (e.g., 50-500 amu) repetitively during the chromatogram. During the usual mode, the MS spends only a very small fraction of the total scan time focusing ions of each m/e ratio. Thus, most of the information provided by the MS (as much as 95-99%) is not relevant. When the MS is made to focus repetitively on a limited number of ions of known significance, the amount of time spent counting each of the limited number of ions is greater than when all ions are scanned. Sensitivity is thus enhanced. In a library search of mass spectra, very few and only minimally interfering compounds were found.

Levins, et al., (1979) examined methods used for PCB analysis, recommended a procedure, and performed verification testing. Their work was performed because conventional PCB analytical methods are frequently difficult to apply to samples derived from combustion sources or ambient air. Their approach is fully described. It is a GC/MS technique involving the following steps:

- Acquire GC/MS data in PCB subset mass windows large enougth to encompass all isotope clusters.
- Examine selected mass spectra to verify the presence of PCBs by their chlorine isotope abundance patterns.
- Generate mass chromatograms from a single mass chosen to represent each chlorobiphenyl isomer (e.g., mono-, di-, tri-, etc., chlorobiphenyl).
- Integrate areas in each mass chromatogram only in the retention time region corresponding to each chlorobiphenyl isomer.
- Quantitate from selected peaks in Aroclor reference standards or with pure isomers.

Advantages of the techniques for measuring individual isomers are:

- Accuracy is not dependent on correct identification of an Aroclor mixture. Thus, samples altered by a combustion source, weathering, or metabolism can be quantitated as accurately as pure standards.
- They eliminate the additional analytical step of perchlorination and the problem of false positives.

Disadvantages of the technique for measuring individual isomers are:

- There is a reduction in sensitivity relative to GC-ECD. Repetitive scanning GC/MS can involve a sensitivity loss of 10^3-10^5 (Eichelberger, et al., 1974). Selective ion monitoring (Eichelberger, et al., 1974 and Levins, et al., 1979) results in an increase in sensitivity, but GC/ECD is still more sensitive.
- GC/MS analyses are considerably more expensive than GC/ECD analyses.

A.5.3 Recommended Method

It is recommended that the methodology specified in EPA's Interim guide (EPA, 1978) be employed for analyses of samples taken during PCB Trial Burns. The Florisil trap or polyurethane foam (sample or blank) trap is extracted with hexane in a soxhlet, cooled, and then concentrated to about 5 ml. Contents of the first two (water filled) impingers are extracted with hexane, dried by passing through columns filled with anhydrous Na_2SO_4, and added to the Florisil extract. The probe and impingers are rinsed with acetone then hexane. The rinses are dried with anydrous Na_2SO_4 and added to the combined extracts. The combined extracts are then cleaned by extracting with concentrated H_2SO_4 (if the cleaned extract is still colored, liquid chromatography on Florisil can be used). Samples of solid and liquid streams are similarly extracted with hexane. Extracts are made to 25 ml volume and split into four portions: three 5-ml volumes for perchlorination and one 10-ml aliquot for confirmation studies by GC/MS. After perchlorination, the solution is extracted four times with hexane and made to 5 ml. Analysis for decachlorobiphenyl is performed by GC-ECD. Chromatographic parameters are:

- Chromatograph - Any suitable instrument.
- Detector - Electron capture, ^3H or ^{63}N.
- Column - 1.8 m x 2 mm ID, 3% OV-210 on Supelcoport, 100/120 mesh.
- Temperatures - Column 280^{o}C, others not specified.
- Carrier gas - Not specified (N_2 or He), 30 ml/min.
- Detection limit - Not specified, but standards of 25 to 50 pg/μl are suggested. The overall detection limit is specified as 10 ng DCB in a 5 ml perchlorination aliquot. This indicates a minimum detection limit of 2 pg/μl injected.

Results are reported in terms of ng DCB per cubic meter of combustion gas, per liter of liquid, or per kg of solid sampled. GC/MS is used to verify the presence of PCBs by pattern matching with Aroclor mixtures. The precision of the DCB analysis is stated to be 10-15%, and recovery of PCBs through the entire sampling and analysis procedure is stated to be 85-95% (EPA, 1978).

It must be repeated that the perchlorination procedure is subject to false positives. Therefore, the importance of adequate test strategy and procedural (sampling and analysis) and reagent blanks cannot be overstated.

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